QUALITATIVE ANALYSIS

TEST AND McLAUGHLIN

	K	Na	NH$_4$	Mg	Ca	Sr	Ba	Zn	Mn	Co	Ni	Al
Cl	32.95 3.9	35.86 5.42	10° 33.0 ——	55.81 5.1	73.19 5.4	51.09 3.0	37.24 1.7	203.9 9.2	150.0 ——	50.0 ——	s.	400
NO$_3$	30.34 2.6	83.97 7.4	200 ——	74.31 4.0	121.8 5.2	66.27 2.7	8.74 0.33	117.8 4.7	v. s.	45.47 5.4	50 ——	v. s.
SO$_4$	11.11 0.62	16.83 1.15	76.0 ——	35.43 2.8	0.20 0.015	0.011 $0.0_3 6$	$0.0_3 23$ $0.0_4 10$	53.12 3.1	43.3 ——	36.21 4.0	106.0 ——	36.1
OH	142.9 18.0	116.4 21.0		0.001 $0.0_3 2$	0.17 0.02	0.77 0.063	3.7 0.22	$0.0_3 5$ $0.0_4 5$	ins.	ins.	ins.	ins.
S	v. s.	s.	s.	hyd.	hyd.	hyd.	hyd.	$0.0_3 69$ $0.0_4 71$	$0.0_3 62$ $0.0_4 72$	$0.0_3 38$ $0.0_4 42$	$0.0_3 36$ $0.0_4 4$	hyd.
CO$_3$	108.0 5.9	19.39 1.8	100 ——	0.1 0.01	0.0013 $0.0_3 13$	0.0011 $0.0_4 7$	0.0023 $0.0_3 11$	0.004 $0.0_3 3$	ins.	ins.	——	hyd.
PO$_4$	25.0	20.0	(sec) 25.0	——	0.015 $0.0_3 5$	ins.	ins.	——	——	ins.	——	ins.
CrO$_4$	63.1 2.7	61.21 3.30	29.0 ——	73.0 4.3	0.4 0.03	0.12 0.006	$0.0_3 35$ $0.0_4 14$					
C$_2$O$_4$	30.27 1.6	3.34 0.24	4.2 ——	0.03 0.0027	$0.0_3 55$ $0.0_4 43$	0.0046 $0.0_3 26$	0.0085 $0.0_3 38$	$0.0_3 64$ $0.0_4 4$	——	ins.	——	ins.

Note. Upper numbers in each square are grams of anhydrous salt in 100 grams of water at ordinary temperature (18°). Lower numbers are molar solubilities.

SOLUBILITIES

Cr	Fe	Cd	Bi	Cu	Pb	Hg^{II}	As	Sb	Sn	Hg^{I}	Ag
ins.	(ic) 158.0 —	140.0 —	hyd.	60.0 —	1.49 0.05	7.4 —	s.	910 —	270 —	0.0_45 0.0_68	0.0_313 0.0_59
—	s.	143 —	hyd.	125	51.66 1.4	hyd.	—	—	—	s.	213.4 8.4
s.	(ous) 60.0 —	s.	hyd.	20.0 —	0.0041 0.0_313	hyd.	—	—	18.8	sl. s.	0.55 0.020
ins.	(ous) 0.0007 0.0_48	0.00026 0.0_518	ins.	ins.	0.01 0.0_34	0.0051 0.0_322	—	—	ins.	ins.	0.01 0.001
hyd.	0.0_362 0.0_47	0.0_313 0.0_59	0.0_418 0.0_635	0.0_434 0.0_535	0.0_492 0.0_536	0.0_513 0.0_754	0.0_452 0.0_521	0.0_347 0.0_552	ins.	—	0.0_414 0.0_655
hyd.	ins.	ins.	—	ins.	0.0_31 0.0_43	—	—	—	ins.	—	0.003 0.0_31
—	ins.	—	—	—	0.0_414 0.0_617	—	—	—	—	—	0.0_364 0.0_416
—	—	—	—	—	0.0_42 0.0_65	ins.	—	—	—	ins.	0.0025 0.0_315
—	v. s.	0.0033 0.0_317	—	—	0.0_316 0.0_554	—	—	—	—	—	0.0034 0.0_371

Where exact figures are not given, s. means "soluble"; v. s., "very soluble"; sl. s., "slightly soluble"; ins., "insoluble"; hyd., "hydrolyzed."
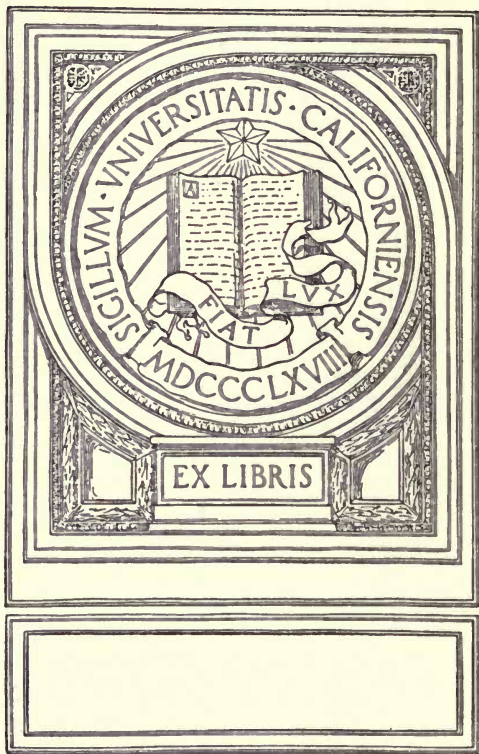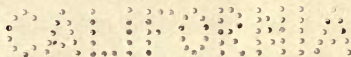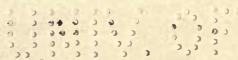
NOTES ON
QUALITATIVE ANALYSIS

BY

LOUIS AGASSIZ TEST

AND

H. M. McLAUGHLIN

PREFACE

Every instructor will be governed in his teaching of a subject by the object to be attained from the course, the time which can be devoted to the work, and his method of presentation.

Qualitative analysis has a place in a beginning course in general chemistry only as a means of reviewing principles already studied and fixing them in the mind of the student by applications.

When qualitative analysis must be given in the first year before the general chemistry is completed, it is frequently difficult to know how to distribute the time between the two subjects. In such cases the instructor must be guided not only by the time he can devote to the work but by the preparation of his students. Most of the texts on qualitative analysis are based on the assumption that the student has completed a course in general chemistry, and are not adapted to students who have had but one semester of general chemistry.

In preparing this outline for their own students the authors have had in mind the preparation of a manual which their students, having had only one semester of general chemistry, could cover in six hours a week for the fifteen weeks available for the course. No excuses are made for the book other than that the authors have found it helpful in their work at Iowa State College and more satisfactory than any they have been able to secure.

The questions given at the end are intended to cover the work given in the manual and to teach the student to think for himself. Some are probably too difficult for the average

student in the time which may be at his disposal, but such questions may easily be omitted at the discretion of the instructor.

In preparing this manual frequent recourse has been had to various larger and more complete texts, and the authors feel particularly indebted to Professors Stieglitz and Treadwell and Hall, which indebtedness they wish to acknowledge.

Thanks are also due to the assisting staff of Iowa State College, all of whom have given much help in trying out these notes with classes.

Particularly do the authors wish to thank Dr. W. A. Roberts, who wrote much of the original notes, Miss Nellie Naylor, and Mr. R. E. Kirk for many helpful suggestions.

CONTENTS

NOTES ON
QUALITATIVE ANALYSIS

INTRODUCTION

Qualitative analysis treats of the identification of substances. In a general qualitative analysis the problem may be the identification of a compound, an element, or some radical or group of elements. This outline deals with the identification of the more common metals and a few of the important nonmetallic radicals. These latter occur as negative ions in acids. A substance is identified by some property which it possesses. The more characteristic and perceptible to our senses this property is, the more certain is the identity of the substance, and if more than one such property can be made use of, so much more positive is the identification. In general we make use of physical properties. These may sometimes be observed in mixtures, but more frequently it is necessary to separate the substance from most or all other material with which it may be found. Such separations are almost always brought about or made possible by chemical means. While physical properties mostly serve for identification, it is frequently necessary to make use of chemical reactions in order that the element or radical may enter into some combination having properties sufficiently distinctive for identification. Such reactions as may cause a change in color, formation of a precipitate, dissolving of a precipitate,

formation of a gas, distinctive odor, etc., are spoken of as tests. A few examples will illustrate:

If to a solution of some unknown substance a few drops of a solution of potassium thiocyanate is added and a deep blood-red color is produced, it is considered proof that ferric iron was in the unknown substance. If sodium chloride is held in a colorless flame a bright-yellow color is imparted to the flame. This is used as a means for the identification of sodium. If strontium chloride is held in a colorless flame a bright-red color is imparted to the flame. This may be used as a means for the identification of strontium. The formation of a precipitate under certain conditions is an important means of identification. If to a solution of some unknown substance a solution of sodium chloride is added, and a white precipitate forms which is insoluble in cold water, it will probably be either lead chloride, mercurous chloride, or silver chloride, lead, mercury, and silver being the only ordinary substances that behave in this manner. If this precipitate dissolves in ammonium hydroxide the substance is most probably a silver salt. If it turns black on the addition of ammonium hydroxide the substance is a mercury compound.

Since most of the reactions used in identification are double decomposition reactions taking place in solution, a brief review of the nature of solution and the ionic theory will be taken up. As most double decomposition reactions in solution are reversible, the idea of equilibrium will play an important part in the discussion.

SOLUTIONS

"A solution may be defined as a body of homogeneous character whose composition may vary between certain limits" (Smith). In order to understand more clearly the technical terms applied to solutions and also their meaning, the following definitions are given. It is customary to speak of a

substance which, like water, forms the bulk of the solution as the *solvent*. The substance which is dissolved is called the *solute*. The amount of substance which is dissolved in a certain quantity of the solvent may vary between wide limits with some substances, while with others it is more limited. A solution which contains a small portion of the dissolved body is spoken of as *dilute*. A solution that contains large amounts of the dissolved substance is called a *concentrated solution*. The amount of material contained in a given volume of solution is spoken of as the *strength* of that solution. The terms *dilute* and *concentrated* do not tell exactly the amount of substance in solution. For more exact work it is necessary to use solutions the exact strength of which can be defined. A convenient standard frequently taken is one gram-molecule of the substance dissolved in enough water to make the total volume one liter. This solution would be of one molar concentration. A solution that contained one tenth of a molecular weight in enough water to make the total volume one liter would be one-tenth molar.

The freezing point of pure water is $0°$ centigrade, and its boiling point at 760 mm. pressure is $100°$ centigrade. If some nonvolatile substance is dissolved in pure water, the freezing point of the solution is found to be below $0°$ and its boiling point is above $100°$, the change being proportional to the amount of solute in a given volume. It was shown by Raoult in 1886 that in dilute solutions of different substances, of the same molar strength, the boiling points of the different solutions would be raised the same amount for each substance. Molar solutions of cane sugar ($C_{12}H_{22}O_{11} = 342$ g.) or glycerin ($C_3H_8O_3 = 92$ g.) in water will each have a boiling point of $100.52°$. If the temperature at which these two solutions freeze is measured, it is found to be $-1.86°$ in each case. If the solutions are half molar, the boiling point will be $100.26°$ and the freezing point $-0.93°$. Other measurements

on solutions of various strengths will show the elevation of the boiling point and the depression of the freezing point to be proportional to the molar strength of the solutions. Solutions of the same molar strength of all substances that are nonvolatile and whose solutions do not conduct electricity behave as glycerin and cane sugar.

Avogadro's hypothesis states that equal volumes of all gases under the same conditions of temperature and pressure contain the same number of molecules. As the gram-molecular weight of any gas always occupies the same volume (22.4 liters), it follows that all gram-molecular weights contain the same number of molecules; hence all molar solutions contain the same number of particles in equal volumes of solution. The change in freezing point and boiling point is, therefore, proportional to the number of molecules, or particles of solute in a given volume of solution.

Experimental results show that some molar solutions give abnormally large changes of freezing and boiling points, and that these are the only solutions which conduct electricity. If an electric current is passed through such a solution it is found that the metallic part of the molecule will collect around the negative electrode (cathode), and the nonmetallic part will collect around the positive electrode (anode). This would lead us to think that the molecule is in some manner dissociated into parts in the solution. It is believed that one of these divisions of the molecule carries a positive electric charge, and the other a negative electric charge, or they would not be attracted to the oppositely charged electrodes. These charged divisions of the molecule are called *ions*. This dissociation in solution is shown almost exclusively by acids, bases, and salts, and such substances are called *ionogens*. The molecule of sodium chloride on this basis would divide into two parts, $NaCl \rightleftarrows Na^+ + Cl^-$. If all of the molecules are dissociated at the same time, a solution would

contain twice as many ions as the number of molecules of undissociated salt. Since the freezing-point lowering and the boiling-point elevation are proportional to the concentration of particles in solution, a solution of sodium chloride would give twice the freezing-point depression and boiling-point elevation that solutions of the same molar strength of cane sugar show. Experiments show that in very dilute solutions this is approximately true. Magnesium chloride shows the possibility of dissociating into three parts ($MgCl_2 \rightleftharpoons Mg^{++} + Cl^- + Cl^-$). Very dilute solutions show approximately three times the normal value. These values, however, are never quite twice or three times the normal but approach these limits as the solutions become more dilute. Hence we assume that only a part of the molecules are broken up at any one time. The following table shows approximately the percentage of molecules ionized in a few solutions of various strengths:

DILUTION	HCl	H_2SO_4	$HC_2H_3O_2$	NaCl
.1 N	92	61	1.3	84
.01 N	96	83	4.1	93
.001 N	100	98	11.6	98

The fact of evaporation indicates that the molecules of a liquid as well as the molecules of a gas are in motion. If we assume that the molecules of a liquid are in motion, then we have a plausible explanation for the evaporation of a liquid as well as other phenomena shown by liquids. In the collisions and jostlings of the moving molecules some will acquire velocities greater than the average velocity. Some of these molecules, because of their unusual velocity, will break away from the attraction of their neighbors and fly off into the space above the liquid. If a current of rapidly moving air is blown across the surface of the liquid, the

escaping molecules will be carried away, causing evaporation to be more rapid. If the liquid is placed in a closed vessel the molecules cannot escape from the inclosed space, and some of them, by collision with other molecules and the walls of the vessel, will be deflected back to the surface of the liquid and condensed. As the concentration of molecules above the liquid increases, the number of these collisions will increase, thus causing the number of molecules returning to the liquid in a given time to increase. A condition must finally result in which the number returning to the liquid in a given time is just equal to the number escaping from the liquid in the same length of time. When this condition exists and equilibrium is established, and the space above the liquid said to be saturated with the liquid vapor, the vapor phase must remain constant, because the number of molecules added to the vapor in a given time is equal to the number taken away in the same length of time. *Evaporation has not ceased, but evaporation and condensation are going on at the same rate.* If the space above the liquid is suddenly increased the equilibrium is destroyed until enough molecules have vaporized to bring the concentration of the vapor again to the saturated condition. If the space is suddenly decreased, equilibrium is destroyed and will be reëstablished only when enough molecules have condensed to bring the concentration of the vapor again to the saturated condition. When two opposing reactions are in equilibrium, so that any change in conditions tends to favor one reaction or the other, such a *reaction is said to be reversible.* Thus the evaporation of water is reversible, and may be represented by the equation,

$$H_2O \text{ (liquid)} \rightleftharpoons H_2O \text{ (vapor)}.$$
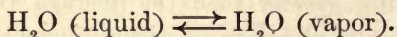
Similarly to the evaporation of a liquid, the process of a solid dissolving in a liquid may be considered to be a diffusion of the molecules of the solid among the molecules of

the liquid. Since numerous collisions will take place, some of the molecules will be deflected in such a manner as to return to the solid, while others will be diffused through the liquid in all directions. With most substances it is possible to increase the concentration of the molecules in solution to such an extent that the number returning to the solid in a given time will just equal the number diffusing away from the solid in the same time. Under such a condition equilibrium will exist between the solid and its solution:

$$\text{Solid} \rightleftarrows \text{solution.}$$

If a nonvolatile substance, such as sodium chloride, is dissolved in water, and the water removed gradually by evaporation, the concentration of the salt in solution must increase. When the concentration has reached a certain value some of the salt will appear in the solid form. This means that the concentration of the dissolved salt is so great that the number of molecules that tend to go to the solid form in a given time is greater than the number that would be dissolved in the same time, thus resulting in the removal of some of the dissolved salt by the formation of the solid. If water is added to the solution, equilibrium will be displaced in the opposite direction and the solid will go into solution. This reaction is then reversible:

$$\text{NaCl (solid)} \rightleftarrows \text{NaCl (dissolved).}$$
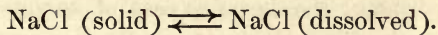
Some of our most familiar chemical reactions are easily reversible. If we pass steam through a tube containing heated iron filings the following reaction occurs:

$$3 \text{ Fe} + 4 \text{ H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + 4 \text{ H}_2;$$
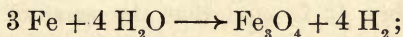
and the hydrogen may be collected over water. If we pass hydrogen over heated iron oxide this reaction takes place:

$$\text{Fe}_3\text{O}_4 + 4 \text{ H}_2 \longrightarrow 3 \text{ Fe} + 4 \text{ H}_2\text{O.}$$
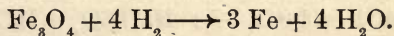
These reactions are the reverse of each other and apparently are contradictory it will be observed.

Why will not the hydrogen and iron oxide formed in the first equation react and reverse that equation? The answer is that they do. If hydrogen and iron oxide are sealed up in a tube and heated, we find that iron and water vapor are formed but that there is also some iron oxide and hydrogen left. Similarly, if iron and water vapor are heated in a sealed tube, hydrogen and iron oxide are formed, but much of the iron and water vapor exists uncombined. Indeed, if the two tubes are heated to the same temperature under the same conditions, the weight of each product in one tube would be the same as the weight of the corresponding product in the other tube.

The explanation is that in one tube the hydrogen and iron oxide begin to react to form iron and water vapor, but that as soon as these substances are formed they in turn react with each other to form hydrogen and iron oxide again. In the other tube the hydrogen and iron oxide formed react to form iron and water vapor, so that in each tube both reactions are going on at the same time. Just as in the evaporation and condensation of water, there must be a point at which these two opposing reactions exactly balance each other. When steam is passed over iron for the purpose of obtaining hydrogen, the large excess of steam used carries along with it the comparatively small amount of hydrogen formed, and the reverse reaction is not noticeable. In passing hydrogen over iron oxide there is a large excess of hydrogen compared with the amount of steam formed, and the reverse action is slight. It is seen that the *mass* of the steam or hydrogen determines the direction of the reaction.

When hydrogen chloride is prepared by the reaction,

$$NaCl + H_2SO_4 \longrightarrow NaHSO_4 + HCl,$$
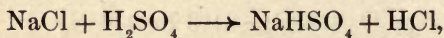
the action apparently goes to completion, and the final products are sodium hydrogen sulfate and hydrogen chloride. If, however, hydrogen chloride is added to a strong solution of sodium hydrogen sulfate a copious precipitate of sodium chloride is produced, showing that the reaction,

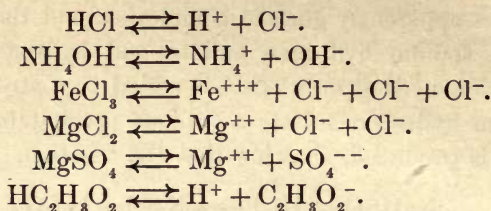$$NaHSO_4 + HCl \longrightarrow NaCl + H_2SO_4,$$
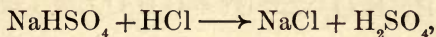
has taken place. The first reaction must therefore be reversible, but under the conditions existing when hydrogen chloride is prepared, the speed in one direction must be far greater than in the other. This is easily explained when it is remembered that hydrogen chloride is a gas, and at the temperature at which the reaction is usually carried out is practically insoluble, hence none is left in contact with the sodium hydrogen sulfate to reverse the reaction.

From these examples it is easily seen that the direction of a reversible reaction depends upon the concentrations of the reacting substances. This is known as the *Mass Law* of Guldberg and Waage, which they stated as follows: *The speed of a reaction is proportional to the concentrations of the reacting substances.*

By a study of the table of ionization with dilution given on page 5, it will be seen that ionization varies with dilution. With greater dilution more of the molecules are constantly in the form of ions, while with more concentrated solutions the amount of ionization is less. According to the idea of reversibility the reaction of an ionogen dissociating into its ions is reversible. For example, sodium chloride dissociates into its ions, and the ions recombine with a certain velocity depending on their concentration according to the equation,

$$NaCl \rightleftharpoons Na^+ + Cl^-.$$
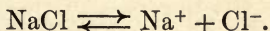
The following are some typical equations showing the ionization in solution of a few familiar acids, bases, and salts:

$$HCl \rightleftarrows H^+ + Cl^-.$$
$$NH_4OH \rightleftarrows NH_4^+ + OH^-.$$
$$FeCl_3 \rightleftarrows Fe^{+++} + Cl^- + Cl^- + Cl^-.$$
$$MgCl_2 \rightleftarrows Mg^{++} + Cl^- + Cl^-.$$
$$MgSO_4 \rightleftarrows Mg^{++} + SO_4^{--}.$$
$$HC_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-.$$

There is great variation shown in the degree to which these substances are ionized in solutions of the same molar concentration.

When equilibrium is established between hydrogen chloride and its ions in a .1 molar solution, about 90 per cent of the molecules are dissociated into ions. In a .1 molar solution of acetic acid about 1.3 per cent is dissociated into the form of ions. A study of the properties of these acids shows that hydrochloric acid is a strong acid, while acetic acid is a weak acid. It is found in every instance that strong acids are those that are highly ionized, while the weak acids are those that are poorly ionized. Similarly, the strong bases are the bases that are highly ionized, while the weak bases are those that are poorly ionized. Very nearly all salts are well ionized and to about the same degree. The following table gives the approximate ionization of various acids and bases in .1 molar solutions:

	PERCENTAGE IONIZED		PERCENTAGE IONIZED
NaOH	90	$H(SO_4^-)$	61
KOH	90	$HC_2H_3O_2$	1.3
NH_4OH	1.3	$H(HS)$	0.1–0.2
HCl	90	$H(HCO_3)$	0.1–0.2
HNO_3	90	HCO_3^-	.005
$H(HSO_4)$	90	HS^-	0.0001

From the foregoing discussion it is evident that when an ionogen is dissolved in water the solution does not consist merely of the molecules of the substance in water, but is

really more complex, containing also the ions into which the salt dissociates. Thus a solution of sodium chloride will contain NaCl molecules, Na^+ ions, and Cl^- ions; a solution of potassium nitrate KNO_3 molecules, K^+ ions, and NO_3^- ions: a solution of sulfuric acid H_2SO_4 molecules, H^+ ions, HSO_4^- ions, and SO_4^{--} ions. Frequently we have to take into consideration also the fact that water is *very slightly* dissociated into H^+ ions and OH^- ions.

In reactions between ionogens in solution all of these substances must be taken into consideration.

When chemical reactions take place between ionogens in solution the reaction is generally a double decomposition reaction. Reactions of this type always take place by the dissociation of the molecules into ions, and the ions recombining in other combinations forming other molecules than the original. If solutions of sodium chloride and potassium nitrate are mixed the reactions will take place according to the following equation:

$$NaCl \rightleftharpoons Na^+ + Cl^-$$
$$KNO_3 \rightleftharpoons NO_3^- + K^+$$
$$\Updownarrow \qquad \Updownarrow$$
$$NaNO_3 + KCl.$$
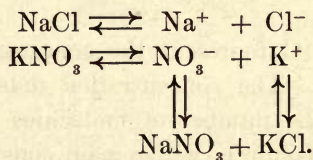
It follows from the Mass Law that the proportion of each substance in the solution after mixing depends upon the concentrations of the various ions. *Concentration* means the amount in unit volume without regard to the total quantity present.

If ferric chloride and potassium thiocyanate solutions are mixed, a deep blood-red compound of ferric thiocyanate is formed:

$$FeCl_3 + 3\ KCNS \rightleftharpoons Fe\ (CNS)_3 + 3\ KCl.$$

This reaction is reversible. If to the solution some solid KCl is added, it will dissolve, increasing the concentration of KCl in the solution, which will cause the reverse reaction

to take place. This will decrease the red $Fe(CNS)_3$, and consequently the color of the solution will become lighter. If, on the other hand, the concentration of either $FeCl_3$ or KCNS is increased by adding more of either substance, the amount of $Fe(CNS)_3$ increases and the color deepens.

In any reversible reaction a definite relation is found to exist between the concentrations of the reacting substances and the products of the reaction. This can be stated in the following mathematical terms. The product of the concentrations of the reacting substances divided by the product of the concentrations of the resulting substances is equal to a constant quantity. If any concentrations are changed, the other concentrations will change in such a manner that the above condition will still hold true. The condition for equilibrium in the reaction of ferric chloride and potassium thiocyanate is expressed by the equation,

$$\frac{C_{FeCl_3} \times C^3_{KCNS}}{C^3_{KCl} \times C_{Fe(CNS)_3}} = K,$$

where the factors C represent the concentrations of the reacting substances. The concentration must be raised to a power equal to the number of molecules of the substance considered. The factor K will remain constant for different concentrations of the reacting components. With sodium chloride in aqueous solution the chemical equation would be $NaCl \rightleftarrows Na^+ + Cl^-$, and the mathematical equation for a condition of equilibrium would be

$$\frac{C_{Na^+} \times C_{Cl^-}}{C_{NaCl}} = K,$$

where C_{Na^+} represents the concentration of the sodium ion, C_{Cl^-} the concentration of the chlorine ion, and C_{NaCl} the concentration of the non-ionized molecules. The constant K is called the *ionization* or *dissociation constant*. For a highly

dissociated substance, as sodium chloride, the constant varies considerably with change of concentration, but holds very closely for little-ionized substances.

If 3.5 grams of ammonium hydroxide is dissolved in enough water to make a liter of solution, experiments show when equilibrium is established that 1.31 per cent of the 3.5 grams is in the form of ions, while 98.69 per cent is in the form of non-ionized molecules:

$$NH_4OH \underset{98.69\%}{\overset{}{\rightleftharpoons}} \underset{1.31\%}{NH_4^+} + \underset{1.31\%}{OH^-}.$$
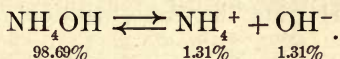
As the gram-molecular weight of ammonium hydroxide is 35, this solution is .1 molar. The molar concentration of the ions will be $(0.1 \times .0131) = 0.00131$ molar; the molar concentration of the non-ionized molecules will be $(0.1 \times .9869) = 0.09869$ molar. Substituting these values in the equation,

$$\frac{C_{NH_4^+} \times C_{OH^-}}{C_{NH_4OH}} = K,$$

$$\frac{0.00131 \times 0.00131}{0.09869} = K = 0.000017+.$$

Thus the value of K is found to be 0.000017+.

In a solution containing 0.35 grams of ammonium hydroxide per liter (0.01 molar), 4.07 per cent is in the form of ions and 95.93 per cent is in the form of non-ionized molecules. Substituting these values in the equation,

$$\frac{(0.01 \times 0.0407) \times (0.01 \times 0.0407)}{0.01 \times 0.9593} = K = 0.000017+;$$

thus the value of K is found to be the same as for a 0.1 molar solution. If many solutions of varying concentrations of ammonium hydroxide are measured, the values of K obtained from all will be found, within the limits of ordinary experimental work, to be 0.000018. As already stated, this rule holds for all slightly ionized or difficultly soluble ionogens

in aqueous solution, each ionogen showing its own particular constant which is different from all others.

The concentration in the dissociation-constant equation represents the total concentration of that particular ion or molecule, regardless of whether it comes from one or more substances that are in solution. Thus in a solution containing NH_4OH and NH_4Cl the value of the concentration of the NH_4^+ ion is made up of the concentration of the NH_4^+ ion from NH_4OH plus the concentration of the NH_4^+ ion from NH_4Cl.

If to a 0.1 molar solution of ammonium hydroxide some strongly ionized ammonium chloride is added, the concentration of the NH_4^+ ion is greatly increased and K becomes greater than 0.000017+. Equilibrium can only be established when the OH^- ions have so far decreased by combining with NH_4^+ ions that K again equals 0.000017+. As the basic properties of ammonium hydroxide, or any base, are due to the OH^- ions which it contains, the addition of NH_4^+ ions (from NH_4Cl or any other ammonium salt) makes ammonium hydroxide appear as a weaker base because of the corresponding decrease in OH^- ions.

Similarly, acetic acid ($H \cdot C_2H_3O_2$), which ionizes

$$H \cdot C_2H_3O_2 \rightleftarrows H^+ + C_2H_3O_2^-,$$
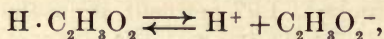
may be made to appear as a weaker acid by adding sodium acetate ($Na \cdot C_2H_3O_2$), which increases the $C_2H_3O_2^-$ ions in solution and correspondingly decreases the H^+ ion characteristic of acids. The concentration of any ion in a solution, then, may be decreased by adding an excess of the other ion into which the substance dissociates. Similarly, the concentration of any ion in a solution may be increased by removing the other ion into which the substance dissociates. Ions may be removed from a solution by causing them to combine to form insoluble or little-ionized substances.

The rule for bringing reactions to completion by forming insoluble, volatile, or little-ionized substances depends on this fact.

The direction in which an ionic reaction will proceed can be predicted if the degree of ionization and the solubility of the reaction compounds are known. In the reaction of sodium hydroxide and hydrochloric acid the reaction will go practically to completion in the direction which results in the formation of water — a very little-ionized substance:

$$Na^+ + OH^- + H^+ + Cl^- \rightleftarrows H_2O + Na^+ + Cl^-.$$
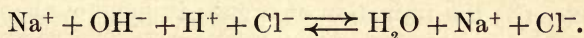
The sodium hydroxide and hydrochloric acid are highly ionized, and the ions formed recombine in another combination to form water and sodium chloride. If water ionizes into hydroxyl ions and hydrogen ions, and sodium chloride is also ionized, there would be no reason to think that these ions would not recombine to form sodium hydroxide and hydrochloric acid, thus making the reaction reversible. However, water gives exceedingly few ions; hence the formation of sodium hydroxide and hydrochloric acid is possible only to a very slight extent. The reaction must then go practically to completion in the direction which results in the formation of water. In the reaction of silver nitrate and hydrochloric acid the reaction will go practically to completion with the formation of silver chloride and nitric acid:

$$Ag^+ + NO_3^- + H^+ + Cl^- \rightleftarrows AgCl + H^+ + NO_3^-.$$
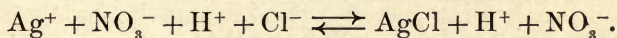
The reason why this reaction goes to completion is that silver chloride is insoluble. The silver ions and the chlorine ions will be removed from solution in the formation of the insoluble silver chloride, and therefore cannot take part in the reverse reaction. In the reaction of hydrochloric acid on calcium carbonate the reaction will go to completion with the formation of calcium chloride, water, and carbon dioxide:

$$2\,HCl + CaCO_3 = CaCl_2 + H_2CO_3\,(H_2O + CO_2).$$
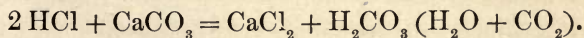
Carbonic acid is formed, which decomposes into carbon dioxide and water, thus removing the carbonate ions and hydrogen ions from solution. In these three illustrations it is shown that the condition under which an ionic reaction goes to completion is the formation of some compound that for one or more of three reasons does not give ions in quantity enough to cause the reaction to go in the reverse direction. These three conditions are (1) the formation of a substance that does not ionize, (2) the formation of a substance that is insoluble, (3) the formation of a gas. In none of these cases can the reaction be said to go absolutely to completion, because water is slightly ionized, silver chloride is very slightly soluble, and carbonic acid is not completely decomposed at ordinary temperature. Reactions of this type are said to go to completion because the reverse action is so slight that it does not interfere in ordinary work.

If a solution of sodium acetate is treated with hydrochloric acid, the reaction will reach equilibrium when very nearly all of the acetate ions are combined with hydrogen ions and very few are free in the solution:

$$HCl + NaC_2H_3O_2 \rightleftharpoons NaCl + HC_2H_3O_2.$$
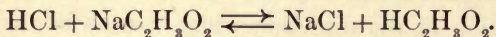
The reason for this is because acetic acid is the least ionized of any of the reacting substances present, as shown by the following ionization constants:

$$\frac{H^+ \times Cl^-}{HCl} = \text{greater than } 1. \quad \frac{Na^+ \times C_2H_3O_2^-}{NaC_2H_3O_2} = \text{approximately } .5.$$

$$\frac{Na \times Cl}{NaCl} = \text{greater than } 1. \quad \frac{H^+ \times C_2H_3O_2^-}{HC_2H_3O_2} = 0.000018.$$
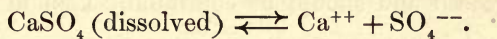
In a reaction where a strong acid acts on the salt of a weaker acid, the salt of the weak acid will be decomposed when the weak acid gives fewer ions to the solution than its salt.
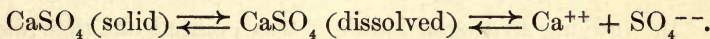
SOLUBILITY-PRODUCT PRINCIPLE

When water is added to solid calcium sulfate the salt will dissolve to a limited extent. If an excess of solid salt is used, equilibrium will result between the solid salt and its solution:

$$CaSO_4 \text{ (solid)} \rightleftarrows CaSO_4 \text{ (dissolved)}.$$
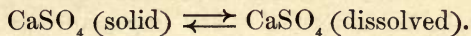
The dissolved salt is in equilibrium with its ions:

$$CaSO_4 \text{ (dissolved)} \rightleftarrows Ca^{++} + SO_4^{--}.$$

The complete equation is

$$CaSO_4 \text{ (solid)} \rightleftarrows CaSO_4 \text{ (dissolved)} \rightleftarrows Ca^{++} + SO_4^{--}.$$

The ionization constant equation for calcium sulfate is

$$\frac{Ca^{++} \times SO_4^{--}}{CaSO_4} = K_2.$$

In a saturated solution the concentration of the solute remains constant at a given temperature. The concentration of undissociated molecules also remains constant. The above equation may then be written for a saturated solution

$$\frac{Ca^{++} \times SO_4^{--}}{CaSO_4} = \frac{Ca^{++} \times SO_4^{--}}{K_1} = K_2, \text{ or } Ca^{++} \times SO_4^{--} = K_2 \times K_1.$$

Since the product of two constants is a constant, then

$$Ca^{++} \times SO_4^{--} = K.$$

Stated in words, *in saturated solutions of difficultly soluble salts the product of the concentration of the ions equals a constant value. This is the solubility-product principle.* A saturated solution of strontium sulfate contains 0.00062 moles per liter, 85 per cent of which is ionized. The concentration of $Sr^{++} = SO_4^{--}$ would be $0.00062 \times 0.85 = 0.0005$.

$$Sr^{++} \times SO_4^{--} = (0.0005)^2 = 0.00000025.$$

If the product of strontium ions and sulfate ions in solution exceeds this value, the ions in excess will combine to form

undissociated molecules, and if the solution is saturated, some of the undissociated molecules must separate out of solution as solid strontium sulfate. Whenever the product of the concentration of the ions exceeds the value of the solubility product constant precipitation will occur unless a supersaturated solution is formed. The importance of these principles, and their application to analysis, will become evident as we proceed and should be continually kept in mind.

HYDROLYSIS

In studying hydrogen iodide it was pointed out that phosphorous iodide and water react to form hydrogen iodide and phosphorous acid:

$$PI_3 + 3\ H_2O = 3\ HI + P(OH)_3.$$
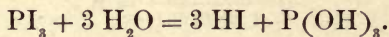
This type of reaction was called hydrolysis.

If normal sodium carbonate (Na_2CO_3) is dissolved in distilled water, the solution will react alkaline to litmus, but if normal copper sulfate ($CuSO_4$) is dissolved in distilled water, the solution reacts acid to litmus. These facts are easily understood when it is remembered that water is very slightly dissociated into hydrogen and hydroxyl ions:

$$H_2O \rightleftharpoons H^+ \times OH^-.$$
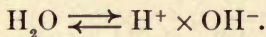
The amount of this dissociation is approximately one gram molecule in ten million liters of water. In consequence of this ionization, although it is extremely small, water will enter into double decomposition reactions with other ionogens. It follows that when normal sodium carbonate is dissolved in water a reaction will take place,

$$Na_2CO_3 + 2\ HOH \rightleftharpoons 2\ NaOH + H_2CO_3,$$
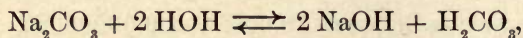
sodium hydroxide and carbonic acid being formed in equal amounts. Although water is very little ionized, and the

reaction proceeds very slightly toward the right, some sodium hydroxide and carbonic acid are formed. Sodium hydroxide is a strong base and gives many hydroxyl ions, while carbonic acid, being a very weak acid, gives few hydrogen ions. It is evident there are more hydroxyl ions in the solution than there are 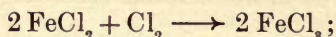hydrogen ions, which will cause the solution to react alkaline. For the same reason, sodium acetate ($NaC_2H_3O_2$), calcium sulfide (CaS), and many other salts show alkaline reaction when dissolved in water. Copper sulfate when dissolved in water reacts according to the following equation,

$$CuSO_4 + 2\ HOH \rightleftarrows Cu\ (OH)_2 + H_2SO_4.$$
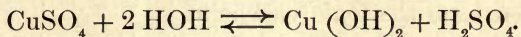
As in the case of sodium carbonate and water, the reaction proceeds very slightly to the right, but equal amounts of copper hydroxide and sulfuric acid are formed. Copper hydroxide is almost insoluble and a weak base and so gives few hydroxyl ions, while sulfuric acid is easily soluble and a very strong acid, giving many hydrogen ions. The excess of hydrogen ions over the hydroxyl ions causes the solution to react acid to litmus. Other salts which react acid for the same reason when dissolved in water are aluminium chloride ($AlCl_3$), zinc sulfate ($ZnSO_4$), mercury nitrate ($Hg(NO_3)_2$), etc. If the salt that is dissolved in water is formed from an acid and a base, both of which are highly ionized, hydrolysis will not take place to the extent it would if the acid or base, or both, were slightly ionized, because the concentration of hydrogen and hydroxyl ions from the strongly ionized acid and base tends to depress the ionization of water; also, as both acid and base are ionized to about the same extent, the solution will react neutral. Sodium chloride may be taken as an example of this class. If both the acid and the base that form the salt are slightly ionized, hydrolysis will be marked.

OXIDATION AND REDUCTION

The definitions of oxidation as the addition of oxygen to an element or compound, and of reduction as the removal of oxygen from a compound, express incompletely what is meant by these terms. Oxidation, more broadly speaking, is an increase in the positive valence of an element or radical, while reduction is a decrease in the positive valence or an increase in the negative valence. If chlorine is added to a solution of ferrous chloride, a reaction takes place in which the ferrous iron is changed to ferric iron,
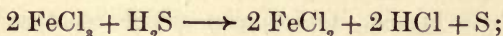
$$2\,FeCl_2 + Cl_2 \longrightarrow 2\,FeCl_3;$$

or, written from the ionic viewpoint,

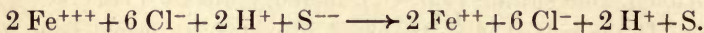$$2\,Fe^{++} + 4\,Cl^- + Cl_2 \longrightarrow 2\,Fe^{+++} + 6\,Cl^-.$$
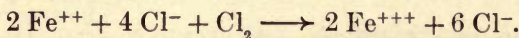
The two ferrous ions have each gained a positive charge, while the chlorine molecule has now become two negatively charged ions. The positive valence of the iron ion has thus increased from two to three. This is oxidation of ferrous iron.

If ferric chloride is treated with hydrogen sulfide in acid solution, the following reaction takes place:

$$2\,FeCl_3 + H_2S \longrightarrow 2\,FeCl_2 + 2\,HCl + S;$$

or, written from the ionic viewpoint,

$$2\,Fe^{+++} + 6\,Cl^- + 2\,H^+ + S^{--} \longrightarrow 2\,Fe^{++} + 6\,Cl^- + 2\,H^+ + S.$$

A positive charge from each ferric ion, and the two negative charges of the sulfur ion, have neutralized each other. The iron has thus had its positive valence reduced from three to two and the sulfur has been changed from a sulfur ion to a sulfur atom. This is reduction of ferric iron, and the sulfur has been oxidized.

According to the electronic theory an atom is made up of a positively charged nucleus surrounded by negatively charged corpuscles. The negative corpuscles are called electrons. In the ordinary atom the amounts of positive electricity

and negative electricity are the same. If an atom loses an electron, the atom will then carry an excess of positive electricity. The loss of one electron will result in the atom's having one positive charge. For example, the sodium ion is a sodium atom minus an electron. If there is a loss of two electrons a double positive charge will result, as in the calcium ion (Ca^{++}). If an atom gain an electron it will become negatively char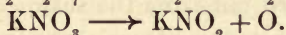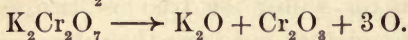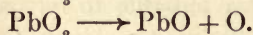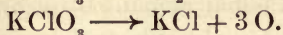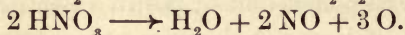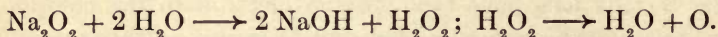ged, as the chlorine ion. If sodium chloride is dissolved in water an electron from the sodium goes to the chlorine, thus giving a positive sodium ion and a negative chlorine ion. The ease with which an element will gain or lose an electron is a property of that element. Thus, in the oxidation of ferrous chloride to ferric chloride by chlorine, the ferrous ions have each lost an electron to the chlorine, which gives the iron an added unit of positive electricity and charges the chlorine with an equal amount of negative electricity. In the reduction of ferric chloride to ferrous chloride by hydrogen sulfide, the sulfur ion has lost two electrons, and each ferric ion has gained one from the sulfur. A study of the electromotive series of metals shows that for the most common metals, beginning with potassium, the tendency to hold electrons increases according to the position in the series: K, Na, Ba, Sr, Ca, Mg, Al, Mn, Zn, Cd, Fe, Pb, H, Cu, Hg, As, Pt, Ag. Any one of these metals will take electrons from any of the metals preceding it in the series. If a solution of copper sulfate is treated with metallic zinc, the copper ion (Cu^{++}) will take two electrons from the zinc atom, causing the zinc to go into solution as the zinc ion (Zn^{++}), while the copper will be reduced by these electrons and be precipitated as metallic copper:

$$Zn + Cu^{++} + SO_4^{--} = Zn^{++} + Cu + SO_4^{--}.$$
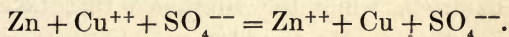
The nonmetallic elements as a rule have the property of taking up electrons and forming negative ions. The metallic

elements have the property of losing electrons and forming positive ions. The ionization of ionogens in solution are examples of these properties.

It is not necessary that oxidation and reduction result in the formation of ions. The rusting of iron, the combination of hydrogen and oxygen, and other reactions of this nature are oxidation reactions. The so-called active nonmetallic elements — those that have a very strong tendency to take up electrons, such as oxygen and chlorine — are most often used as oxidizing agents. The following equations show some of the substances that may be used to furnish oxygen and the method in which they may be considered to decompose to furnish the oxygen :

$$Na_2O_2 + 2\,H_2O \longrightarrow 2\,NaOH + H_2O_2 ;\ H_2O_2 \longrightarrow H_2O + O.$$
$$2\,HNO_3 \longrightarrow H_2O + 2\,NO + 3\,O.$$
$$KClO_3 \longrightarrow KCl + 3\,O.$$
$$PbO_2 \longrightarrow PbO + O.$$
$$K_2Cr_2O_7 \longrightarrow K_2O + Cr_2O_3 + 3\,O.$$
$$KNO_3 \longrightarrow KNO_2 + O.$$

An illustration of the action of nitric acid as an oxidizing agent is its effect on hydrochloric acid. A mixture of these two acids is called aqua regia :

$$2\,HNO_3 \longrightarrow H_2O + 2\,NO + 3\,O,$$
$$6\,HCl + 3\,O \longrightarrow 3\,H_2O + 6\,Cl.$$
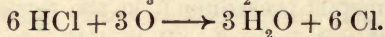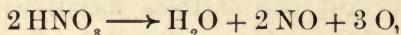
It should be kept in mind that the oxidation of a substance cannot take place without the reduction of other substances. All reactions that are spoken of as oxidation reactions are also reduction reactions. The substance that loses the electrons is oxidized, while the substance that takes up the electrons is reduced. Most oxidation and reduction reactions are conveniently written in steps. All the oxidation reactions attempted in this outline will be written in the simplest

manner in which they may be considered to take place. Whenever possible, the oxidizing agent will be considered to break up in such a manner as to furnish free oxygen, and the compound to be oxidized to decompose into the oxide of the element concerned. This oxide will then be acted upon by the free oxygen to form the oxidized product. To illustrate:

When manganese hydroxide is oxidized by sodium peroxide the reactions may be assumed to be

$$Na_2O_2 + 2 H_2O \longrightarrow 2 NaOH + H_2O_2,$$
$$H_2O_2 \longrightarrow H_2O + O ;$$
$$Mn (OH)_2 \longrightarrow MnO + H_2O ;$$
$$MnO + O \longrightarrow MnO_2.$$
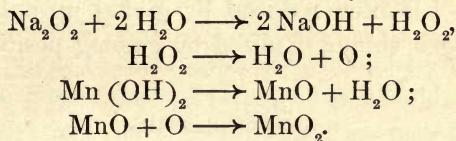
If the oxide formed is an anhydride it will probably combine with water to form an acid or a base. For example,

$$SO_2 + O \longrightarrow SO_3,$$
$$SO_3 + H_2O \longrightarrow H_2SO_4.$$
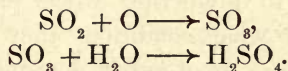
If it is a hydrogen compound which is oxidized, the free oxygen from the oxidizing agent will usually combine with the hydrogen, forming water, thus freeing the radical combined with the hydrogen, which may combine with other radicals in the solution, either of the same or different kinds. As illustrations may be cited the action of nitric acid on hydrochloric acid to form free chlorine, as given above, two chlorine atoms uniting to form a molecule; also the action of nitric acid on hydrogen sulfide:

$$2 HNO_3 \longrightarrow H_2O + 2 NO + 3 O,$$
$$3 H_2S + 3 O \longrightarrow 3 H_2O + 3 S.$$
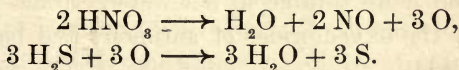
If this reaction is considered from the point of transfer of charges, it is seen that nitrogen in changing from valence 5 in HNO_3 to valence 2 in NO loses three positive charges, or

$2 N^{+++++} \longrightarrow 2 N^{++} + 6 \oplus$. The $6 \oplus$ oxidizes $3 S^{--}$ to free sulfur. This can be represented as follows:

$$2 HNO_3 \longrightarrow H_2O + 2 NO + 3 O^{--} + 6 \oplus ;$$
$$3 H_2S \longrightarrow 6 H^+ + 3 S^{--} ;$$
$$6 H^+ + 3 O^{--} \longrightarrow 3 H_2O ;$$
$$6 \oplus + 3 S^{--} \longrightarrow 3 S.$$
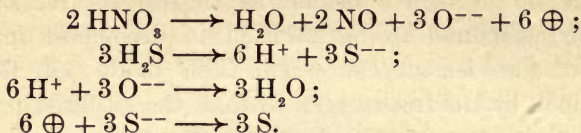
The oxygen, being charged negatively, combines with the hydrogen, which is positively charged, to form water. Thus the nitric acid has been reduced by giving up positive charges, and hydrogen sulfide oxidized by gaining positive charges.

Solubilities

A general knowledge of the solubility of salts and other compounds frequently used in qualitative analysis is of great value as an aid to predicting when precipitates may be formed and under what conditions they will be dissolved. It will also often be a great aid in determining possible compounds in a mixture.

The following are given as a few simple general rules of solubilities of compounds:

All sodium, potassium, and ammonium compounds are soluble.

All normal nitrates are soluble; all normal acetates are soluble.

All chlorides are soluble except silver chloride, mercurous chloride, and lead chloride. The latter is slightly soluble in cold water and more soluble in hot water. Some basic chlorides, notably the oxychlorides of antimony and bismuth, are difficultly soluble.

All sulfates are soluble except the sulfates of lead, barium, strontium, and calcium, the latter being slightly soluble.

With few exceptions other compounds are insoluble in water. These include oxides, hydroxides, carbonates, sulfides, phosphates, silicates, tartrates, oxalates, etc.

These general rules, if remembered, will often be very useful in the course of an analysis. For example, if barium has been found in an unknown mixture which is soluble in water, the sulfate radical cannot be present and need not be tested for. Similarly, if the chloride ion is found in a soluble mixture, silver ions cannot be present. When greater detail in regard to the solubility of particular compounds is desired, some of the numerous tables of solubilities may be consulted.

A few exceptions to these general rules will be noted when met with (see Exp. 1, Alkali Group). It should always be borne in mind that even soluble substances may differ very greatly in their degree of solubility, and that increase in temperature generally, but not always, increases solubility. Hydrolysis may sometimes cause the formation of basic or acid salts which show a different solubility from the corresponding normal salts. Examples are the chlorides of antimony and bismuth and the sulfides of the alkaline earth metals.

General Instructions

Cleanliness is essential to success in chemical analysis. All apparatus should be thoroughly washed, then rinsed with distilled water before it is used or before it is put away. Observe all reagents that are used, and if not clear they should be filtered. From 1 cc. to 5 cc. is sufficient unless an excess is called for. In neutralizing solutions or making them acid or alkaline, great care should be taken to assure thorough mixing before testing with litmus, as otherwise only a part of the solution may be neutralized. *Acidity or alkalinity should never be taken for granted, but a test should always be made.* Prepare a wash bottle for distilled water, and keep it always filled ready for use. Distilled water must be used exclusively

except in washing glassware. Prepare three stirring rods by sealing the ends of a glass tube about the length of a lead pencil, or by fire-polishing the end of a glass rod. Also prepare two glass tubes about six inches long and fire-polish both ends.

Precipitation is effected by the formation of an insoluble compound from a solution. This is usually accomplished by adding a reagent which reacts by double decomposition to form an insoluble product with the ions it is desired to remove from the solution. The precipitated solid may be crystalline or amorphous. It may rise to the surface of the liquid or sink to the bottom of the vessel. For rapid precipitation the solutions should be stirred and heated except where heat would produce undesired reactions. The latter are the exception. In most reactions a large excess of the precipitant should be avoided, but the presence of a slight excess is requisite when complete precipitation is desired. To prove that an excess of the precipitant has been used, let the precipitate settle, or filter a little, and add a few drops of the precipitant to the clear solution. If a precipitate forms, not enough of the precipitant has been added. If complete precipitation is not desired, but formation of an insoluble compound only to be observed, addition of the reagent need not be continued after a permanent precipitate forms.

Filtration consists in separating a liquid from a solid by pouring the mixture on a filter that is porous enough to permit the passage of the liquid but will retain the solid. Sometimes the solid is so finely divided that it will pass through the filter. In some instances this may be remedied by heating the mixture for some time and filtering through two thicknesses of filter paper. Where a precipitate is not crystalline, rapid filtration is best performed by allowing the precipitate to settle and then pouring off the supernatant liquid as completely as possible, transferring the precipitate to the filter afterwards. The process of pouring off the supernatant liquid
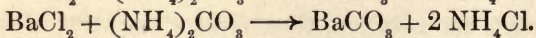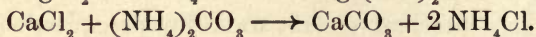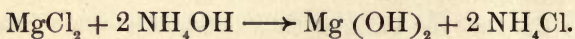
is *decantation.* Heating, where permissible, will often help to settle a precipitate more quickly by causing coagulation.

All precipitates collected on a filter are washed at least twice with distilled water or with such reagents as may be called for in the instructions. It is very necessary that all precipitates collected on a filter be carefully washed with water unless there are specific instructions to the contrary. If this washing is not thoroughly carried out it frequently happens that some of the solution, containing metals to be tested for later, will be retained by the precipitate in sufficient quantity to interfere seriously with the identification of metals contained in the precipitate. Unless otherwise stated, the washing is best performed with hot water. In washing a filter it should never be filled more than two thirds full of precipitate. After the solution has drained off, a small stream of water from the wash bottle should be directed into and around the filter just below the top in such a manner as to force the precipitate towards the point of the filter. Great care should be used *never* to add enough water to fill the filter to the top. The liquid is allowed to drain out completely, and the washing repeated as often as necessary to remove all soluble material. Time may often be saved by allowing the precipitate to settle and pouring off the supernatant liquid through the filter, retaining the precipitate in the beaker. Water is then added to the residue in the beaker, and, after settling, the liquid again decanted through the filter. This may be repeated three or four times, if desired, before the residue is washed into the filter. *All precipitations with hydrogen sulfide must be carried out in a closed vessel.* A small Erlenmeyer flask, with a one-hole stopper fitted with a six-inch glass tube, serves very well. For precipitation, remove the stopper and allow a few bubbles of hydrogen sulfide to pass through the solution, then replace the stopper and shake the vessel. If a reaction takes place the gas will be absorbed,

causing the pressure in the flask to decrease, and more gas passes into the solution as it is needed. An arrangement of this type prevents the escape of the gas into the room.

The ability to make a satisfactory analysis depends largely upon being able to recognize a reaction by the color, form of precipitate, etc., that is characteristic of the different substances studied. Description alone will not enable one to recognize a substance or a reaction. Preliminary experiments are given which are illustrative of all the reactions that will take place in the analysis of an unknown substance by the outline. Close attention must be paid to the nature of all precipitates, colors, etc., and these observations recorded briefly. The notes should be recorded in a tabular form and equations written for all reactions. Below is an example covering a few experiments on the alkaline earth group:

	CALCIUM	BARIUM	STRONTIUM	MAGNESIUM
Reagent NH_4OH	No precipitate	No precipitate	No precipitate	$Mg(OH)_2$, white, soluble in weak acids and ammonium chloride
Reagent $(NH_4)_2CO_3$	$CaCO_3$, white, insoluble in NH_4Cl, soluble in $HC_2H_3O_2$	$BaCO_3$, white, insoluble in NH_4Cl, soluble in $HC_2H_2O_2$	$SrCO_3$, white, insoluble in NH_4Cl, soluble in $HC_2H_3O_2$	$MgCO_3Mg(OH)_2$, white, soluble in NH_4Cl and $HC_2H_3O_2$
Flame	Brick red	Green	Crimson	
Etc.				

$$MgCl_2 + 2\,NH_4OH \longrightarrow Mg\,(OH)_2 + 2\,NH_4Cl.$$
$$CaCl_2 + (NH_4)_2CO_3 \longrightarrow CaCO_3 + 2\,NH_4Cl.$$
$$SrCl_2 + (NH_4)_2CO_3 \longrightarrow SrCO_3 + 2\,NH_4Cl.$$
$$BaCl_2 + (NH_4)_2CO_3 \longrightarrow BaCO_3 + 2\,NH_4Cl.$$
Etc.

In the study of qualitative analysis the student must constantly remember that merely following the directions mechanically brings no practical knowledge of the subject. All experiments and tests should be conscientiously made and all observations carefully recorded. Through applying the knowledge of chemistry already gained strive to understand the reason for each step and to interpret and write each reaction. Only in this way will any real advance be made. In the laboratory cleanliness, patience, and care will be found invaluable. Strict honesty with yourself towards your work is as necessary here as elsewhere. The student who is not thoroughly conscientious will gain nothing. Directions should be carefully read and understood before beginning each part of the work and then accurately followed.

For the purpose of qualitative analysis the metals are divided into groups, each group including metals that behave similarly with certain reagents. The classification is based on the formation of insoluble compounds with certain reagents called group reagents. The following is the classification used in this outline:

Silver group. Metals whose chlorides are *insoluble* in cold water or dilute acids: lead, silver, and mercurous mercury.

Arsenic group. Metals whose sulfides are *insoluble* in dilute acids but are *soluble* in yellow ammonium sulfide: arsenic, antimony, and tin.

Copper group. Metals whose sulfides are *insoluble* in dilute mineral acids and in yellow ammonium sulfide: copper, bismuth, cadmium, lead, and mercuric mercury.

Iron-zinc group. Metals whose sulfides are *soluble* in dilute mineral acids but are *insoluble* in ammoniacal solution: nickel, cobalt, iron, chromium, aluminium, manganese, and zinc.

Alkaline earth group. Metals that will not be precipitated by the reagents used for the preceding groups but will be precipitated as carbonates in the presence of ammonium chloride:

barium, calcium, strontium. Magnesium will also be considered with this group, though it is not precipitated by the carbonate ion in the presence of much ammonium chloride.

Alkali group. With the exception of magnesium, metals that will not be precipitated by the reagents for any of the above groups : sodium, potassium, and ammonium.

THE ALKALI GROUP

The members of this group to be studied are sodium, potassium, and ammonium. Almost without exceptions the compounds of these ions are soluble in water. Ammonium is classed with this group because the solubility of ammonium compounds is similar to that of sodium and potassium compounds. The identification of sodium and potassium will depend largely upon the color their heated vapors impart to a flame. Ammonium compounds are all decomposed by heat and will all evolve ammonia when heated in strong alkaline solution. On account of the solubility of these compounds the members of this group will remain in solution while all others are removed in the form of insoluble salts.

Use solutions of sodium chloride, potassium chloride, and ammonium chloride in the experiments which follow.

Experiment 1

To a portion of each solution add sodium cobaltinitrite.

Experiment 2

Mix a small amount of ammonium chloride solution with sodium hydroxide solution in a small beaker. Make alkaline. Cover the beaker with a watch glass on the under side of which is placed a strip of moist red litmus paper. Warm the mixture but do not boil. Notice the change in color of the litmus and the odor of the evolved gas. *Care must be taken to prevent any of the sodium hydroxide from coming in contact with the litmus paper either by spattering or by the paper's touching the sides of the beaker.*

Experiment 3

Place a little solid ammonium chloride in a porcelain crucible and heat to redness over a free flame.

Experiment 4

Heat in a colorless flame sodium, potassium, and ammonium chloride separately by dipping in solutions of each a clean platinum wire and holding the wire in the flame. (Clean the wire carefully each time before placing it in another solution. This may be accomplished by dipping the wire in concentrated hydrochloric acid and holding it in the flame until the flame is colorless.) Observe the flame produced by each through three thicknesses of blue glasses or a color screen. Use a mixture of sodium chloride and potassium chloride and observe if one can be detected in the presence of the other.

THE ALKALINE EARTH GROUP

This group includes calcium, barium, strontium, and magnesium. These metals occur in the third column of the periodic table and are uniformly divalent in their compounds. In general their compounds so resemble each other in color and solubility that the separation for qualitative analysis will depend largely upon the degree of insolubility of certain characteristic compounds. This group will remain in solution with the alkali group until the other groups have been precipitated. Barium, strontium, and calcium are precipitated from magnesium and the alkali group as carbonates. The table on page 32 gives the solubilities of some of the more insoluble salts of the metals of this group together with the corresponding sodium and potassium compounds.

The upper number in each square is the number of grams of anhydrous salt held in solution by 100 cc. of water at 18°. The lower number is the molar solubility.

The table of solubilities shows the hydroxides, with the exception of magnesium hydroxide, to be moderately soluble

in water.   Magnesium hydroxide will be precipitated by ammonium hydroxide, while the other members of the group will remain in solution. This method for the separation of magnesium from the other members of the group is not practical, because precipitation of magnesium as hydroxide is not complete, and may be prevented altogether by the presence of ammonium salts, as ammonium chloride. The reason

	K	Na	Ba	Sr	Ca	Mg
OH	142.9 18	116.4 21	3.7 0.22	0.77 0.063	0.17 0.02	0.0015 0.0002
SO$_4$	11.11 0.62	16.83 1.15	0.00023 0.00001	0.011 0.0006	0.20 0.015	35.43 2.8
CrO$_4$	63.1 2.7	61.21 3.3	0.00035 0.000015	0.12 0.006	0.4 0.03	73.0 4.3
C$_2$O$_4$	30.27 1.6	3.34 0.24	0.0086 0.00038	0.0046 0.00026	0.00056 0.000043	0.03 0.0027
CO$_3$	108.0 5.9	19.39 1.8	0.0023 0.00011	0.0011 0.00007	0.0013 0.00013	0.1 0.01
PO$_4$					MgNH$_4$PO$_4$	0.00086

for this interference with precipitation by ammonium chloride can be explained by the solubility-product principle and the effect on ionization by the addition of a common ion. It will be remembered that in the introduction it was shown how the addition of an ammonium salt to a solution of ammonium hydroxide caused a *marked decrease in the concentration of hydroxyl ions*, due to the excess of ammonium ions added. A 0.1 molar solution of magnesium chloride is 70 per cent ionized, thus making the concentration of the magnesium ion 0.07 molar. The solubility product of magnesium hydroxide is
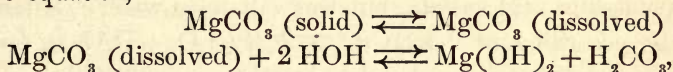
$$C_{Mg} \times C^2_{OH} = 3.4 \times 10^{-11}.$$

Substituting the value of the magnesium ion in 0.1 molar solution in this equation and solving, the concentration of

hydroxyl ion is found to be 0.0000235 molar. The concentration of hydroxyl ions must exceed this value in order that magnesium hydroxide be precipitated from a 0.1 molar solution of magnesium chloride. The concentration of hydroxyl ions in a solution that is 0.1 molar with respect to both ammonium hydroxide and ammonium chloride is 0.000021. Solutions of these concentrations would produce no precipitate of magnesium hydroxide. Calcium, barium, and strontium are precipitated as normal carbonates by ammonium carbonate in the presence of ammonium chloride. Normal magnesium carbonate will not be precipitated by ammonium carbonate even in the absence of ammonium chloride, because of hydrolysis. However, a basic carbonate of varying composition may be precipitated in the absence of ammonium chloride. The composition of the precipitate obtained varies considerably with conditions but might be most simply written

$$MgCO_3 \cdot Mg(OH)_2.$$
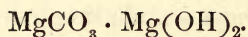
As the hydrolysis is an equilibrium reaction represented by the equation,

$$MgCO_3 \text{ (solid)} \rightleftharpoons MgCO_3 \text{ (dissolved)}$$
$$MgCO_3 \text{ (dissolved)} + 2 HOH \rightleftharpoons Mg(OH)_2 + H_2CO_3,$$

it is seen that the addition of ammonium chloride would decrease the hydroxyl ions and thus prevent the precipitation of the magnesium hydroxide. This will cause the reaction to proceed more rapidly to the right, and the magnesium carbonate would be changed into magnesium hydroxide, which would dissolve.

As the carbonates of barium, strontium, and calcium are much less soluble than magnesium carbonate, and are not readily dissolved by ammonium chloride, the separation of magnesium from the other members of the group will be by the precipitation of the carbonates of barium, strontium, and calcium from an alkaline solution that contains ammonium

chloride. The carbonates of barium, strontium, and calcium are slightly soluble in ammonium salts, especially when heated. On this account a large excess of ammonium chloride should be avoided and the solution should not be boiled. The carbonates are dissolved in acetic acid. Strong acids must not be used because they would interfere with the separation of barium later. Barium is separated from strontium and calcium by precipitating it from the acetic-acid solution as barium chromate by means of potassium dichromate. Potassium dichromate ($K_2Cr_2O_7$) is the acid salt of chromic acid, and is related to potassium chromate (K_2CrO_4) much as potassium acid sulfate ($KHSO_4$) is related to potassium sulfate (K_2SO_4). If potassium acid sulfate is heated, the following reaction takes place:

$$2\,KHSO_4 \longrightarrow K_2S_2O_7 + H_2O.$$
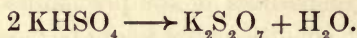
Two molecules of the acid salt lose one molecule of water to form $K_2S_2O_7$, known as potassium pyrosulfate. When to K_2CrO_4 an acid is added, $KHCrO_4$ is formed, as in the case of potassium acid sulfate, but this salt loses water spontaneously, according to $2\,KHCrO_4 \rightleftharpoons K_2Cr_2O_7 + H_2O$, to form *potassium dichromate.* As this reaction is reversible every solution of a dichromate and every acid solution of a chromate contains both CrO_4^{--} and $Cr_2O_7^{--}$ ions. When a barium salt is added to such solution the Ba ions will tend to combine with both the CrO_4^{--} ions and the $Cr_2O_7^{--}$ ions. As $BaCrO_4$ is much less soluble than $BaCr_2O_7$, the CrO_4^{--} ions are constantly removed from the solution and the reaction proceeds toward the left until all the dichromate has decomposed into the chromate or all the barium has been precipitated. Thus the precipitate formed is barium chromate ($BaCrO_4$) even when a dichromate ($K_2Cr_2O_7$) is used as the reagent. Strong acids, by their tendency to form dichromate ions ($Cr_2O_7^{--}$), will prevent the precipitation of barium as chromate.

All precipitates that form in this group should be further tested by the flame. It must be remembered that the separation of the members of this group from each other depends on the difference in solubility of similar compounds, which frequently is not relatively large, and as concentrations often cannot be known it sometimes happens that the precipitate sought may be mixed with that of some other member of the group. In particular this may be the case with barium and strontium when the former is precipitated as chromate. Diluting the solution decreases the possibility of precipitating strontium as chromate. To insure complete separation of barium from strontium and calcium, the solution from which the barium has been precipitated as chromate is treated with ammonium carbonate. This will precipitate the strontium and calcium as carbonates, but will not precipitate any barium left in solution. The carbonates of strontium and calcium are much less soluble than the corresponding chromates; but barium chromate is less soluble than barium carbonate (see table of solubilities, p. 32), hence there are too few barium ions left in the solution, after an excess of chromate ions has been added, to precipitate with the carbonate ion. Upon the same principle depends the identification of strontium and its separation from calcium. Strontium sulfate is so much less soluble than calcium sulfate that the concentration of the sulfate ion in a saturated solution of calcium sulfate will be sufficient to precipitate strontium ions even from a fairly dilute solution of a strontium salt. The sulfate ions being already in solution in combination with calcium ions would precipitate no calcium. Strontium and barium are separated from calcium by adding sulfate ions in moderate concentrations, which removes practically all strontium (and barium) ions from solutions as sulfate. Some calcium is also generally precipitated as sulfate, but a saturated solution of calcium sulfate contains calcium ions enough to precipitate calcium

oxalate on addition of the oxalate ion. Calcium oxalate is much less soluble than calcium sulfate (see table of solubilities, p. 32). As oxalic acid is a weak acid, the presence of any strong acid tends to dissolve the calcium oxalate due to the combination of the hydrogen ions with the oxalate ion.

Calcium cannot be tested for in the presence of strontium, either by the flame test or by precipitation as oxalate. As seen from the table (p. 32), the difference in solubility of calcium and strontium oxalates is so slight that it would be impractical to attempt to prevent the precipitation of strontium with calcium by controlling the concentration of the oxalate ion; hence the separation of the two is necessary.

Strong acids must not be used for dissolving the carbonates, because barium is to be precipitated as chromate, and the salt cannot be precipitated in the presence of a strong acid:

$$2 \, BaCrO_4 + 4 \, HCl = H_2Cr_2O_7 + 2 \, BaCl_2 + H_2O.$$
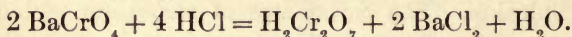
Use solutions of the nitrates or chlorides of barium, strontium, calcium, and magnesium in the experiments which follow.

Experiment 5

Make each solution alkaline with ammonium hydroxide, then add ammonium carbonate. Add to each resulting mixture enough acetic acid to give the solution an acid reaction. Could these precipitates be formed in acid solution?

Experiment 6

Add to each solution an equal volume of ammonium chloride solution, make alkaline with ammonium hydroxide, and add ammonium carbonate. What difference do you observe between these results and those in Experiment 5? Filter each mixture and wash the precipitates in a little warm water by pouring the water over the precipitate collected on the filter and letting it pass through the filter. Dissolve each precipitate in the least amount of acetic acid possible by pouring the acid over the precipitate on the filter. Add a few drops of five per cent potassium dichromate

solution to each filtrate. Test the solubility of any precipitate that forms in hydrochloric acid.

Experiment 7

Heat solutions of each almost to boiling, then add five per cent ammonium sulfate solution, a few drops at a time, until an equal volume has been added. Let the mixtures stand for ten minutes, filter, make the filtrates alkaline by addition of ammonium hydroxide, and then add ammonium oxalate. (See table of solubilities for explanation of results.) Test the solubility of the precipitate in acetic acid and in hydrochloric acid.

Experiment 8

To each solution add an equal volume of a saturated solution of calcium sulfate. Heat to boiling and let stand for ten minutes.

Experiment 9

To a solution of magnesium chloride or nitrate add five times its volume of water, enough ammonium chloride to prevent the precipitation of magnesium hydroxide, make alkaline with ammonium hydroxide, and add disodium phosphate solution. The precipitate formed should be crystalline. If no precipitate forms at first, shake vigorously and let stand for a few minutes.

Experiment 10

Observe the color imparted to a colorless flame by the heated vapors of the chlorides of barium, strontium, and calcium. (See Experiment 4, p. 31.) Observe the colors with and without the blue glasses or color screen.

Notes on Analysis

1. The flame test is best made in hydrochloric acid solution, because the chlorides are more volatile than many other salts. The solutions should be concentrated.

2. In dilute solutions formation of a precipitate may be very slow on account of the formation of supersaturated solutions. In the precipitations of this group considerable time should be allowed before discarding the solutions. If no precipitate forms at first, shake vigorously. Warming sometimes hastens precipitations.

3. When the alkaline earth metals are to be precipitated from a filtrate from which other groups have been removed, it will generally be best to concentrate the solution before adding ammonium carbonate.

SCHEME FOR ANALYSIS OF THE ALKALI AND THE ALKALINE EARTH GROUPS

Solution contains Ca^{++}, Ba^{++}, Sr^{++}, Mg^{++}, NH_4^+, K^+, Na^+

a. Test a small portion of the solution for ammonium according to Experiment 2.

b. Try the flame test for sodium.

c. To a larger portion of the solution add NH_4Cl until addition of NH_4OH gives no precipitate. Make alkaline with NH_4OH and add $(NH_4)_2CO_3$. Heat to 60°–70° for a few minutes, adding a few drops of $(NH_4)_2CO_3$ from time to time. Filter, and test filtrate with $(NH_4)_2CO_3$ to make sure of complete precipitation. Wash the precipitate with hot water.

Precipitate: $BaCO_3$, $CaCO_3$, $SrCO_3$	**Filtrate**
Dissolve in the smallest possible amount of hot dilute acetic acid by pouring the acid repeatedly over the precipitate collected on the filter. Test a small portion of the solution for Ba by adding a few drops of $K_2Cr_2O_7$. Warm the solution. If Ba is present, a precipitate will be formed. If Ba is absent, dilute all of the acid solution to about 10 cc., divide into two parts, and proceed with the analysis for Sr and Ca. If Ba is present, dilute all of the acid solution to about five times its volume. Warm and add $K_2Cr_2O_7$ until the solution is distinctly yellow. Filter, and wash the precipitate with warm water. Analyze precipitate and filtrate as directed on page 39.	Add a few drops of $(NH_4)_2SO_4$ and $(NH_4)_2C_2O_4$; warm and filter if necessary. Divide the solution into two parts. (1) Acidify with HCl. Evaporate to dryness and ignite (heat strongly) until ammonium salts are entirely removed. Dissolve the residue in 3–4 cc. of water to which a few drops of HCl have been added. Filter if not clear and to the solution add $Na_3Co(NO_2)_6$. Confirm a precipitate by the flame test. (2) To the second part, made alkaline with NH_4OH, add Na_2HPO_4. A white crystalline precipitate indicates Mg. Confirm by dissolving in the least amount of HCl possible, heat to boiling, and neutralize with NH_4OH. The precipitate should reappear in a crystalline form.

SCHEME FOR ANALYSIS OF THE ALKALI AND THE ALKALINE
EARTH GROUPS (*Continued from page 38*)

Precipitate : BaCrO₄	Filtrate
Dissolve in a few drops of concentrated HCl and confirm by the flame test. Green flame proves Ba.	Make alkaline with NH_4OH, add $(NH_4)_2CO_3$, warm to 60°–70°, for a few minutes, filter, and reject the filtrate. Wash the precipitate, dissolve in acetic acid, dilute to 10 cc., and divide into two parts. (1) Test one part for Sr by adding an equal volume of $CaSO_4$ solution. Heat and let stand for at least ten minutes. If a precipitate forms, confirm Sr by the flame test. (2) Test the second portion for Ca. If Sr is present, make the solution alkaline with NH_4OH and add an equal volume of $(NH_4)_2SO_4$. Heat for a few minutes, let cool, and filter. Make the filtrate alkaline with NH_4OH and add $(NH_4)_2C_2O_4$. A precipitate insoluble in acetic acid is probably CaC_2O_4. Confirm by the flame test. If Sr is not present the treatment with $(NH_4)_2SO_4$ is omitted.

4. No precipitates will be produced in solutions of calcium, strontium, and barium salts on the addition of ammonium hydroxide if this reagent is free from carbonates. If carbonate is present in the ammonium hydroxide, however, a turbidity may result due to the formation of the carbonates of these metals. This turbidity may also appear when solutions of these metals, after having been made alkaline by the addition of ammonium hydroxide, are allowed to stand, on account of the absorption of carbon dioxide from the air.

5. The identification of the members of this group is made more certain if the spectroscope is used in connection with the flame reactions. By this means the presence of the metals in quantities too small to produce conclusive precipitates may be proved. These tests have not been included in the outline because it is often not feasible to use the spectroscope with large classes.

THE SULFIDE GROUPS

Those metals which in this outline are separated from the metals of other groups by their precipitation as sulfides include mercury (mercuric), lead, bismuth, copper, cadmium, arsenic, antimony, tin, iron, cobalt, nickel, zinc, and manganese. Aluminium and chromium are precipitated in these groups but on account of hydrolysis are not precipitated as sulfides but as hydroxides. If the position of these elements in the periodic table is noted, it is observed that they are scattered through groups I to VIII inclusive and will be expected to vary greatly in their chemical conduct. Some are moderately strong metals, while others show pronounced nonmetallic properties. Most of them show more than one valence, with characteristic properties for each. Many enter easily into complex ions, while others show little such tendency and behave normally in this respect.

This great variation in chemical behavior makes it possible and necessary to subdivide further these metals, after precipitation, into smaller groups, in which identification is more easily carried out.

The reagent used for the precipitation of these metals is hydrogen sulfide. The separation into subdivisions depends primarily upon the concentration of the sulfide ion necessary for the precipitation of the different metal ions. This, in turn, depends upon the concentration of hydrogen ion in the solution, or, in other words, the acidity or alkalinity of the solution, which controls to a very large extent the concentration of sulfide ion which can be present in a saturated solution of hydrogen sulfide. To understand the principle of this separation a careful study of the effect which variation in the acidity of the solution (concentration of H ion) will have upon the sulfide ion is therefore of the greatest importance to the student.
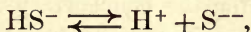
Hydrogen sulfide is a dibasic acid and shows a primary and secondary ionization. The primary ionization,

$$H_2S \rightleftharpoons H^+ + HS^-,$$
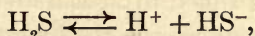
shows an ionization constant

$$(1) \quad \frac{C_{H^+} \times C_{HS^-}}{C_{H_2S}} = K = 0.91 \times 10^{-7},$$

and the secondary ionization,

$$HS^- \rightleftharpoons H^+ + S^{--},$$

shows the constant

$$(2) \quad \frac{C_{H^+} \times C_{S^{--}}}{C_{HS^-}} = K = 1.2 \times 10^{-15}.$$

In a saturated solution of hydrogen sulfide the concentration would be very nearly constant, and at 25° and atmospheric pressure $C_{H_2S} = 0.1$ molar. Substituting this value in equation (1),

$$(3) \quad C_{H^+} \times C_{HS^-} = 0.91 \times 10^{-8}.$$

As the molar concentrations of the H^+ ions and HS^- ions are equal, the value for each would be

$$\sqrt{0.91 \times 10^{-8}} = 0.95 \times 10^{-4}.$$

Multiplying equations $(1) \times (2)$,

$$(4) \quad \frac{C^2_{H^+} \times C_{S^{--}}}{C_{H_2S}} = 1.1 \times 10^{-22}.$$

Substituting in this the value for C_{H_2S} in a saturated solution,

$$(5) \quad C^2_{H^+} \times C_{S^{--}} = 1.1 \times 10^{-23}.$$

Substituting in this the value for C_{H^+} found above,

$$(6) \quad C_{S^{--}} = \frac{1.1 \times 10^{-23}}{(.95 \times 10^{-4})^2} = 1.2 \times 10^{-15}.$$

This last value is the concentration of sulfide ion (S^{--}) in a solution saturated with H_2S at 25° and atmospheric pressure.* If any acid is added to a saturated solution of hydrogen sulfide, the large increase in the hydrogen ions in solution would cause a decrease in the concentration of the sulfur ions. The value for the concentration of the sulfur ions may be found by substituting the molar concentration of the hydrogen ion in equation (5).

The following table shows the values in a saturated hydrogen-sulfide solution for the concentrations of the sulfur ion in the presence of varying amounts of hydrochloric and acetic acids:

MOLECULAR CONCENTRATION OF ACID	PER CENT HCl DISSOCIATED	C_s^{--} IN PRESENCE OF HCl	PER CENT ACETIC ACID DISSOCIATED	C_s^{--} IN PRESENCE OF ACETIC ACID
0.		1.2×10^{-15}		1.2×10^{-15}
0.001	98.7	1.1×10^{-17}	11.62	3.2×10^{-16}
0.01	96.6	1.18×10^{-19}	4.05	6.7×10^{-17}
0.1	91.56	1.5×10^{-21}	1.303	6.5×10^{-18}
0.2	89.3	3.4×10^{-22}	0.917	
0.5	85.38	6.1×10^{-23}	0.5694	1.3×10^{-18}

From the table it is seen that the concentration of the sulfur ion is approximately one millionth (10^{-6}) as large in the presence of 0.1 molar hydrochloric acid as in neutral solution. Since acetic acid is very slightly ionized, it causes very little change in the concentration of the sulfur ion. The following table, taken from Treadwell and Hall's "Qualitative Analysis," gives the solubility and solubility product for the sulfides of a number of metals:

* See Stieglitz, Qualitative Analysis, Vol I, pp. 199-201.

Substance	Grams per Liter	Moles per Liter	Solubility Product
CuS . . .	8.8×10^{-21}	8.2×10^{-23}	$C_{Cu^{++}} \times C_{S^{--}} = 8.5 \times 10^{-45}$
CdS . . .	8.6×10^{-13}	6.0×10^{-15}	$C_{Cd^{++}} \times C_{S^{--}} = 3.6 \times 10^{-29}$
FeS . . .	3.4×10^{-8}	3.9×10^{-10}	$C_{Fe^{++}} \times C_{S^{--}} = 1.5 \times 10^{-19}$
HgS . . .			$C_{Hg^{++}} \times C_{S^{--}} = 4.0 \times 10^{-53}$
MnS . . .	3.3×10^{-6}	3.8×10^{-8}	$C_{Mn^{++}} \times C_{S^{--}} = 1.4 \times 10^{-15}$
NiS . . .	7.0×10^{-11}	1.2×10^{-12}	$C_{Ni^{++}} \times C_{S^{--}} = 1.4 \times 10^{-24}$
PbS . . .	4.9×10^{-12}	2.0×10^{-14}	$C_{Pb^{++}} \times C_{S^{--}} = 4.2 \times 10^{-28}$
ZnS . . .	3.3×10^{-10}	3.5×10^{-12}	$C_{Zn^{++}} \times C_{S^{--}} = 1.2 \times 10^{-28}$
H₂S . . .			$C_{H^{+}} \times C_{S^{--}} = 1.1 \times 10^{-23}$

By substituting in the solubility-product equation for any metallic sulfide the value of $C_{S^{--}}$ found above, the concentration of the metallic ion, which must be present in order to cause precipitation, may be calculated.

To illustrate:

$$C_{Mn^{++}} \times C_{S^{--}} = 1.4 \times 10^{-15};$$

then

$$C_{Mn^{++}} = \frac{1.4 \times 10^{-15}}{1.2 \times 10^{-15}} = 1.16 \text{ moles.}$$

This means that in a neutral solution saturated with hydrogen sulfide the molar concentration of the manganese ion must be 1.16 moles, which is equivalent to 1.16×54.93, or 63.7 grams per liter, before a precipitate of manganese sulfide will be produced. A similar calculation will show that in a neutral solution only 1×10^{-8} moles, or 6.5×10^{-7} grams, of zinc ion must be present in order that a precipitate of zinc sulfide may be produced. For cadmium ion 3×10^{-14} moles, or 3.4×10^{-12} grams per liter, is all that would be required to produce a precipitate of cadmium sulfide.

Making use of the values for C_{s--} in the table on page 42, it is easy to determine the concentration of any metal ion necessary to produce a precipitate in solutions of various strengths of acid. To illustrate: The solubility product for ZnS is $C_{Zn^{++}} \times C_{s--} = 1.2 \times 10^{-23}$. Substituting the value of C_{s--} for 0.2 molar HCl in this equation,

$$C_{Zn} = \frac{1.2 \times 10^{-23}}{3.4 \times 10^{-22}} = 0.34 \times 10^{-1}, \text{ or } 0.034 \text{ moles};$$

or $0.034 \times 65 = 2.2$ grams per liter.

The precipitation of zinc sulfide, even from a solution which was neutral in the beginning, is never complete, however, for the hydrochloric acid which accumulates from the reaction $ZnCl_2 + H_2S \longrightarrow ZnS + 2\ HCl$ furnishes many hydrogen ions, which soon greatly decrease the value of C_{s--}, as can be seen from the table, and bring the precipitation to a standstill. By a similar calculation for cadmium sulfide in 0.2 molar hydrochloric acid solution, the value for $C_{Cd^{++}}$ necessary to produce a precipitate can be shown to be $1 \times 10^{-7} \times 112$, or 0.00001 grams per liter. So if the concentration of the acid did not get above 0.2 molar, cadmium would be practically all precipitated from a solution of any of its salts in a solution saturated with H_2S. These figures show that the ratio between the quantities of cadmium ion and zinc ion necessary to produce a precipitate in 0.2 molar solution of HCl is $1:22000$. Lead sulfide and tin sulfide show about the same solubility as cadmium sulfide, these three being the most soluble sulfides of the copper and arsenic groups. As zinc sulfide is the least soluble sulfide of the iron-zinc group, it is easily seen that in a solution having acid concentration sufficient to prevent the precipitation of zinc sulfide, — and hence sulfides of all other metals of the iron group, — cadmium, lead, and tin sulfides would be practically completely precipitated along with the other sulfides of the copper and

arsenic groups. Regulating the acid concentration, therefore, furnishes a convenient method for the separation of the copper and arsenic groups from the iron-zinc groups, and is the basis for this division. In practice it is found that an acid concentration of 0.25 molar gives a very complete separation of these groups. The approximate concentration of hydrochloric acid in any solution may be determined by means of methyl violet, as will be illustrated later.

The methods for separation of the groups from each other have so far been based chiefly upon physical differences between the groups. Advantage is often taken of the relative difference in solubility of compounds, as, for example, the difference in solubility of the carbonates of the alkali and alkaline earth groups and the difference in solubility of the sulfides of the copper and the iron-zinc groups.

In the separation of the arsenic group from the copper group use is made of chemical differences between the elements in the two groups. So far the elements studied have been decidedly base-forming in their properties. If the position of arsenic, antimony, and tin in the periodic table be noted, it is seen that they are probably more acid-forming than base-forming in their properties. A study of these elements proves this to be the case. As would be expected, the acid-forming properties are especially prominent in the higher valences of these elements. The lower oxides all show some basic-forming tendency (particularly is this true of tin), and even in the higher oxides are seen some base-forming properties, which, however, are very slight. All of these elements form chlorides which, while often much hydrolyzed, nevertheless give enough positive ions in hydrochloric acid solution to be precipitated by hydrogen sulfide. Arsenic is the most strongly acid-forming of this group, and tin the least. It is a well-known fact that oxygen may be replaced by sulfur without any profound change in the chemical nature of the compound.

It would be expected, then, that the sulfides of this group would show acid properties. Advantage is taken of this property to separate these elements from the copper group. Just as carbon dioxide will combine with calcium oxide to form calcium carbonate, so carbon disulfide combines with potassium sulfide:

$$CO_2 + CaO \longrightarrow CaCO_3$$
$$CS_2 + K_2S \longrightarrow K_2CS_3.$$
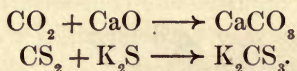
In the same way the sulfides of this group, particularly the higher ones (As_2S_5, Sb_2S_5, SnS_2), and indeed all of the lower sulfides except SnS, will combine with sulfides of the alkali metals to form soluble salts of the thio acids:

$$As_2S_3 + 3\,(NH_4)_2S \longrightarrow 2\,(NH_4)_3AsS_3.$$
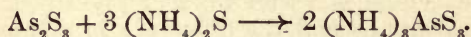
This salt, ammonium thioarsenite, ionizes as follows:

$$(NH_4)_3AsS_3 \rightleftharpoons 3\,NH_4^+ + AsS_3^{---}.$$
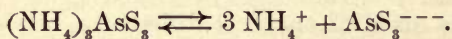
Stannous sulfide is too base-forming to produce thio salts in this way. It is therefore necessary to *sulfurize* it before a complete separation of the arsenic group from the copper group can be accomplished. This is brought about by the use of yellow ammonium sulfide, which contains polysulfides, as $(NH_4)_2S_2$ etc. The action may be represented as follows:

$$SnS + (NH_4)_2S_2 \longrightarrow SnS_2 + (NH_4)_2S$$
$$SnS_2 + (NH_4)_2S \longrightarrow (NH_4)_2SnS_3.$$
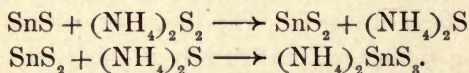
The free thio acids from which these salts are derived are very unstable, breaking up when freed, just as carbonic acid does. If a strong acid be added to a solution containing a thio salt, the sulfide is precipitated as represented by the following equations:

$$(NH_4)_3AsS_3 + 3\,HCl \longrightarrow H_3AsS_3 + 3\,NH_4Cl$$
$$2\,H_3AsS_3 \longrightarrow As_2S_3 + 3\,H_2S.$$
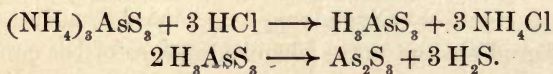
SEPARATION OF ARSENIC, COPPER, AND IRON GROUPS FROM EACH OTHER. REACTIONS OF SULFIDE ION *

Experiment 11

1. Place about 5 cc. of a solution of mercuric chloride in a precipitation flask, add a few drops of dilute hydrochloric acid, heat to boiling, and saturate with hydrogen sulfide. Test the solubility of the precipitate in yellow ammonium sulfide. To do this, filter a little of the solution and test the precipitate by transferring a little of it to a test tube and adding 1 cc. of yellow ammonium sulfide solution. Warm if necessary, filter, and acidify the filtrate with dilute HCl.

2. Repeat 1, using instead of mercuric chloride each of the following solutions: lead acetate, bismuth chloride, copper sulfate, cadmium sulfate, sodium arsenite, antimony chloride, stannous chloride.

Experiment 12

1. Place about 5 cc. of each of the following solutions successively in a precipitation flask, add a few drops of dilute hydrochloric acid, warm, and saturate with hydrogen sulfide as in Experiment 11: ferric chloride, potassium alum, chrome alum, zinc sulfate, cobalt chloride, nickel chloride, manganese sulfate. Does a precipitate form in any case?

2. Using solutions of the same salts as in 1, treat each, without acidifying, with a few drops of ammonium sulfide solution. Note if a precipitate is formed and its color. Save the solutions containing the precipitates.

3. Without filtering or heating, add to each precipitate obtained in 2 an equal volume of dilute hydrochloric acid. If the sulfides do not dissolve readily, leave them in contact with the acid three or four minutes.

4. Tabulate the results obtained in 1. Would you expect all sulfides formed in 2 to be soluble in dilute acid? Explain the results obtained in 3. What use may be made of these results in analysis?

* If time does not permit a study of all the ions in these groups, the instructor may shorten the work by using salts of a few of the typical ions in each group, omitting such others as may seem desirable.

The arsenic and copper groups are best separated from the iron-zinc group by precipitating them in a hydrochloric-acid solution 0.25 to 0.30 molar. As mentioned above, this strength may be determined by means of methyl violet.

Methyl violet in the presence of concentrated hydrochloric acid is yellow, but in the presence of very dilute acid it is blue. As the acid concentration becomes less, the color of the methyl violet changes successively as follows: yellow, greenish-yellow, green, greenish-blue, blue. The concentration of acid which gives a green color with methyl violet, without a tinge of yellow or blue, represents a concentration of 0.25 molar hydrochloric acid, which is the concentration of acid to make a complete precipitation of all the metals in the above list, from arsenic to stannous tin inclusive.

Experiment 13

Make a number of marks on white porcelain (or a piece of white paper) with an indelible pencil (methyl violet). Place 1 cc. of concentrated hydrochloric acid in a beaker. By means of a stirring rod moisten one of the pencil marks with one drop of the acid. Note the color. Now dilute the 1 cc. of concentrated hydrochloric acid, first by adding 5 cc. of water, and then add successively the following amounts: 6 cc., 12 cc., 24 cc., 48 cc. After each dilution moisten one of the indelible pencil marks with one drop of the acid. If the concentrated hydrochloric acid were 12 molar, what would be the molar concentration after each dilution?

Compare the colors of the methyl violet produced by each molar concentration of acid. This test should be used whenever the arsenic and copper groups are to be separated from the iron-zinc group.

THE IRON–ZINC GROUP
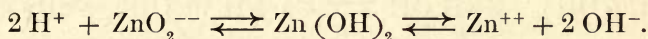
AMPHOTERIC HYDROXIDES

If a solution of sodium hydroxide is added to a solution of a zinc salt, a precipitate of zinc hydroxide will be formed. However, if an excess of sodium hydroxide is used the precipitate will dissolve with the formation of water and sodium zincate according to the equation

$$Zn\,(OH)_2 + 2\,NaOH \longrightarrow Na_2ZnO_2 + 2\,H_2O.$$
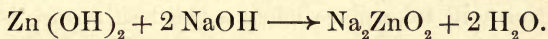
If hydrochloric acid is added to the precipitate of zinc hydroxide, the hydroxide dissolves with the formation of zinc chloride and water:

$$Zn\,(OH)_2 + 2\,HCl \longrightarrow ZnCl_2 + 2\,H_2O.$$
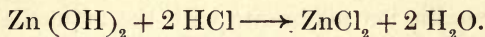
In the reaction of both hydrochloric acid and sodium hydroxide on zinc hydroxide water was one of the products of the reaction. This shows that zinc hydroxide must give hydroxyl ions to combine with the hydrogen ion of hydrochloric acid to form water, and also that zinc hydroxide must give hydrogen ions to combine with the hydroxyl ions of sodium hydroxide to form water. Zinc hydroxide must then ionize both as an acid and as a base:

$$2\,H^+ + ZnO_2^{--} \rightleftharpoons Zn\,(OH)_2 \rightleftharpoons Zn^{++} + 2\,OH^-.$$

In the presence of a strong base zinc hydroxide acts as an acid; in the presence of a strong acid it acts as a base. A hydroxide that ionizes both as an acid and as a base is called an *amphoteric* hydroxide. Many of the elements form hydroxides that show this characteristic to a certain extent. The elements that show this property most prominently are those elements that form neither strong acids nor strong bases. Among these may be mentioned zinc, aluminium, chromium, tin, arsenic, and lead. Further discussion will be given as these examples are met with in analysis.

FORMATION OF COMPLEX IONS

When ammonia gas (NH_3) is passed into water it dissolves, partly by chemical union with the water to form ammonium hydroxide. As a result the following equilibrium exists:
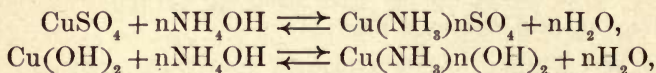
$$NH_3 + H_2O \rightleftharpoons NH_4OH \rightleftharpoons NH_4^+ + OH^-.$$
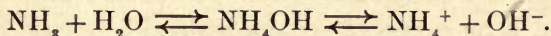
As the solution contains ammonia (NH_3) molecules as well as NH_4^+ and OH^- ions, there is a possibility that more than one reaction will take place when a third substance is added. (1) Double decomposition may take place, resulting in the formation of the metallic hydroxide:
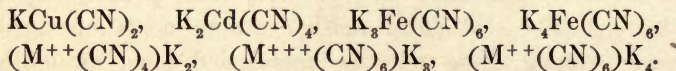
$$CrCl_3 + 3NH_4OH \rightleftharpoons 3NH_4Cl + Cr(OH)_3.$$
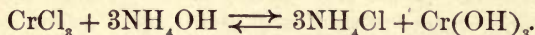
(2) The metallic ion may unite with the ammonia (NH_3) to form a complex ion. The number of ammonia groups (NH_3) which may unite with the metallic ion varies under different conditions of pressure, temperature, etc., but it is usually 2, 4, or 6.

The metals which form complex ions with ammonia are silver, copper, cadmium, cobalt, nickel, and zinc. A few examples will illustrate:

$$CuSO_4 + nNH_4OH \rightleftharpoons Cu(NH_3)nSO_4 + nH_2O,$$
$$Cu(OH)_2 + nNH_4OH \rightleftharpoons Cu(NH_3)n(OH)_2 + nH_2O,$$

where n represents some small number, usually from 2 to 6. The complex ion ($Cu(NH_3)n$) formed is positive and has the same valence as the metallic ion from which it was formed.
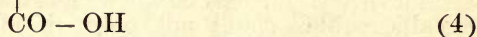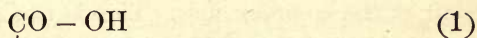
The cyanides of the heavy metals dissolve in an excess of the alkali cyanides to form complex compounds, as shown by the following, where M stands for the metal:

$$KCu(CN)_2, \quad K_2Cd(CN)_4, \quad K_3Fe(CN)_6, \quad K_4Fe(CN)_6,$$
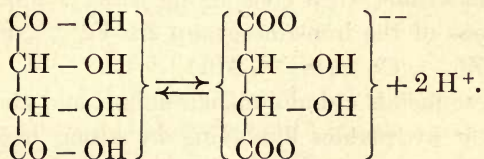$$(M^{++}(CN)_4)K_2, \quad (M^{+++}(CN)_6)K_3, \quad (M^{++}(CN)_6)K_4.$$

Some of the metals which form complex cyanides are silver, gold, copper, cadmium, iron, cobalt, nickel, and zinc.

A separation of copper and cadmium or of cobalt and nickel may be made by the use of these complex cyanides. The potassium salts of hydroferrocyanic acid $(K_4Fe(CN)_6)$ and of hydroferricyanic acid $(K_3Fe(CN)_6)$ are used in making tests for, or in distinguishing between, ferric and ferrous iron.

Certain organic acids have the ability to unite with some metallic ions to form complex ions. The formula for tartaric acid $(H_2C_4H_4O_6)$ is written structurally:
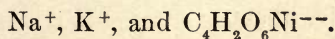
$$
\begin{array}{ll}
CO - OH & (1) \\
CH - OH & (2) \\
CH - OH & (3) \\
CO - OH & (4)
\end{array}
$$

in which hydrogen atoms (1) and (4) split off as ions.

$$
\left.\begin{array}{l}
CO - OH \\
CH - OH \\
CH - OH \\
CO - OH
\end{array}\right\} \rightleftarrows \left\{\begin{array}{l}
COO \\
CH - OH \\
CH - OH \\
COO
\end{array}\right\}^{--} + 2\,H^+.
$$

When ionized in this manner such salts as cream of tartar $KH\,(C_4H_4O_6)$ and Rochelle salts $NaK\,(C_4H_4O_6)$ may be formed. In the presence of a large excess of sodium or potassium hydroxide the hydroxyl groups attached to the CH groups may split off hydrogen ions which can be replaced by certain metals. Nickel and copper ions under these conditions enter easily into the tartrate molecule, as illustrated by

$$
\begin{array}{l}
COONa \\
CH - O \\
{>}Ni, \\
CH - O \\
COOK
\end{array}
$$
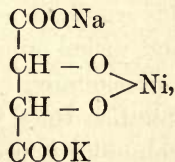
which gives the ions

$$Na^+,\ K^+,\ \text{and}\ C_4H_2O_6Ni^{--}.$$

Such complex ions are quite stable, and in the case of the nickel salt so few nickel ions are given that no precipitate of nickel will be produced in such a solution by hydrogen sulfide. Advantage is sometimes taken of this in the separation of cobalt from nickel.
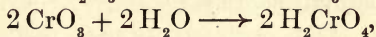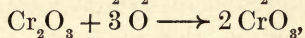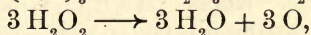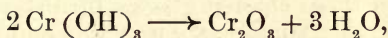
All of these reactions, in which complex ions are formed, are more or less reversible, and hence there is always present in solution of such salts a few of the simple metallic ions as well as the complex ions. This is easily understood when it is remembered that sulfide ion (S^{--}) precipitates zinc, cobalt, nickel, or copper as sulfide from solutions of their salts made alkaline with ammonium hydroxide. This precipitation of the metallic sulfide could not occur if all the metal ion had entered the ammonia molecule to form the complex ion. This fact is important when considering these complex ions.

The ions of the iron-zinc group are Fe^{+++}, Fe^{++}, Al^{+++}, Cr^{+++}, Zn^{++}, Co^{++}, Ni^{++}, Mn^{++}.
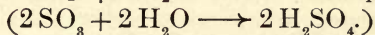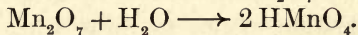
Of these metals aluminium, chromium, and zinc are amphoteric, their hydroxides dissolving in strong bases, and zinc, cobalt, and nickel form complex ions with ammonia. Manganous hydroxide is not amphoteric, neither does manganese form complex ions with ammonia; but being somewhat soluble, manganous hydroxide behaves like magnesium hydroxide and dissolves in ammonium chloride solution, though less readily than the latter. Manganous hydroxide readily combines with oxygen from oxidizing agents, or even from the air, going over into the less soluble hydrated manganese dioxide ($MnO(OH)_2$), and in this condition is not soluble in ammonium chloride. Cobalt and nickel sulfides are peculiar in the fact that while they are precipitated only in neutral or alkaline solution, after precipitation these sulfides are not soluble in dilute acids. This insolubility is probably due to a change which occurs in the sulfides after precipitation. Strong acids or aqua regia dissolve them.

Ferrous hydroxide is somewhat similar to magnesium and manganous hydroxide and is not completely precipitated in the presence of ammonium salts. For its complete separation from manganese it is therefore necessary to oxidize the iron to the ferric condition before precipitation, as the ferric hydroxide is not soluble in ammonium salts.

Chromium and manganese in their highest states of oxidation (chromium six and manganese six and seven) form acids the alkali salts of which are soluble, and whose ions are characteristically colored in solution. It is thus possible to identify these elements in the presence of some others of this group. These oxidations may be illustrated by the following equations, written in steps, showing the oxidation of chromic hydroxide to chromic acid by hydrogen peroxide and the oxidation of manganous sulfate to permanganic acid by oxygen which may be considered as obtained from any sufficiently strong oxidizing agent:

$$2\,Cr\,(OH)_3 \longrightarrow Cr_2O_3 + 3\,H_2O,$$
$$3\,H_2O_2 \longrightarrow 3\,H_2O + 3\,O,$$
$$Cr_2O_3 + 3\,O \longrightarrow 2\,CrO_3,$$
$$2\,CrO_3 + 2\,H_2O \longrightarrow 2\,H_2CrO_4,$$

and
$$2\,MnSO_4 \longrightarrow 2\,MnO + 2\,SO_3,$$
$$2\,MnO + 5\,O \longrightarrow Mn_2O_7,$$
$$Mn_2O_7 + H_2O \longrightarrow 2\,HMnO_4.$$
$$(2\,SO_3 + 2\,H_2O \longrightarrow 2\,H_2SO_4.)$$
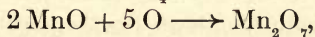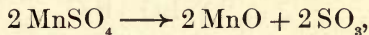
In the first illustration the color of the solution changes from green to yellow, as the chromic ion is green and the chromate yellow. In the second the manganous ion which is almost colorless has been converted into the intensely purple permanganate ion. As CrO_3 is an acid anhydride only, hydrogen sulfide will not precipitate chromium sulfide nor hydroxide from solutions of chromates. It is therefore necessary, if chromium might be present, to reduce any chromate

to a chromic salt before precipitation of the iron-zinc group with ammonium sulfide. The reduction, which must be carried out before iron is oxidized, may be accomplished in acid solution by any good reducing agent, as hydrogen sulfide, sulfur dioxide, alcohol, etc. This is illustrated by the reduction of potassium dichromate to chromic sulfate by hydrogen sulfide in sulfuric acid solution:

$$K_2Cr_2O_7 \longrightarrow K_2O + 2\,CrO_3,$$
$$2\,CrO_3 \longrightarrow Cr_2O_3 + 3\,O,$$
$$3\,O + 3\,H_2S \longrightarrow 3\,H_2O + 3\,S\,;$$
$$Cr_2O_3 + 3\,H_2SO_4 \longrightarrow Cr_2(SO_4)_3 + 3\,H_2O\,;$$
$$K_2O + H_2SO_4 \longrightarrow K_2SO_4 + H_2O.$$
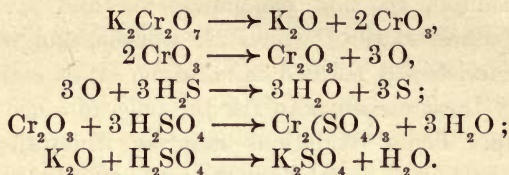
The color of the solution changes from the orange of the dichromate ion to the green of the chromic ion.

Most of the metals of this group when fused with borax impart a characteristic color to the borax glass so formed. In many cases these colored glasses furnish satisfactory tests for the elements. Borax ($Na_2B_4O_7$) may be considered as made up from two molecules of sodium meta-borate and one molecule of boric anhydride thus:

$$2\,NaBO_2 \cdot B_2O_3.$$
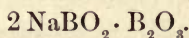
Like other acid anhydrides, boric anhydride is capable of combining with metallic oxides to form salts, as

$$CuO + B_2O_3 \longrightarrow Cu(BO_2)_2.$$

The reaction of cobalt in the borax bead might then be written:

$$2\,NaBO_2 \cdot B_2O_3 + CoO \longrightarrow 2\,NaBO_2 \cdot Co(BO_2)_2.$$
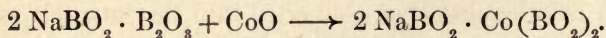
This compound is intensely blue.

SEPARATION AND IDENTIFICATION OF THE MEMBERS OF THE IRON-ZINC GROUP

Before beginning the following experiments review the results obtained in Experiments 12 and 13, pages 47–48.

Experiment 14

1. To 5 cc. of ferric chloride solution add a drop or two of ammonium hydroxide, shake, and then add an excess of this reagent (see page 50). Now add 2 cc. of ammonium chloride solution and observe if any change occurs.

2. Repeat 1, using solutions of potassium alum, chrome alum, cobalt chloride, nickel chloride, zinc sulfate, and manganese sulfate instead of ferric chloride.

3. Repeat 1 and 2, using sodium hydroxide in place of ammonium hydroxide and omitting the ammonium chloride. Note how the results in 3 differ from those obtained in 1 and 2 and explain.

Experiment 15

Add sodium hydroxide to a chrome alum solution until the precipitate first formed is dissolved. Now add about 1 gram of sodium peroxide and boil until all the peroxide is decomposed. Notice, and account for, the change in color. Acidify one half of this solution with sulfuric acid and introduce hydrogen sulfide until the color is changed. Acidify the other half of the solution with acetic acid and divide it into two parts. To one part add barium chloride solution and to the other lead acetate. Explain all reactions.

Experiment 16

1. Prepare some aluminium hydroxide and fuse a portion of it with sodium carbonate on a piece of platinum foil (or a piece of charcoal may be substituted for the platinum) which is held in the oxidizing portion of a blowpipe flame. Moisten the white fused mass with one drop of cobalt nitrate solution and fuse again.

2. Repeat 1, using any zinc salt instead of the aluminium hydroxide. Compare the two results.

Experiment 17

1. Take three portions *each* of ferric chloride solution and freshly prepared ferrous ammonium sulfate solution. To one portion of each add potassium ferrocyanide solution; to a second, potassium ferricyanide solution; and to the third, potassium thiocyanate solution. Note carefully the colors in each case.

2. Repeat 1, using three portions of a ferric chloride solution which has been acidified with hydrochloric acid and has had hydrogen sulfide passed through it for a few minutes.

3. Repeat 1, using a solution of ferrous ammonium sulfate which has been boiled for a few minutes with 1 cc. of concentrated nitric acid. Explain the results.

SCHEME FOR ANALYSIS OF THE IRON-ZINC GROUP *

Besides the metallic ions of this group the solution may contain the metallic ions of the alkaline earth and alkali groups.

Warm the solution, add NH_4Cl and NH_4OH until, after shaking, the solution smells strongly of ammonia. Keep near the boiling point and saturate with H_2S. Filter; wash as quickly as possible with water containing a little $(NH_4)_2S$ to prevent oxidation. Test filtrate with $(NH_4)_2S$ to make sure all of group is precipitated. If the filtrate is brown, an excess of $(NH_4)_2S$ has been used and some nickel sulfide has dissolved. In this case boil the brown filtrate with acetic acid and filter through a fresh filter.

Filtrate contains metals of alkaline earth and alkali groups and after boiling off H_2S is reserved to be tested for these groups (see page 38).

Precipitate: $Al(OH)_3$, $Cr(OH)_3$, Fe_2S_3, FeS, MnS, ZnS, CoS, NiS
Remove precipitate from the filter and treat with 15-25 cc. of dilute HCl (dilute acid of the laboratory and an equal volume of water), grinding the precipitate with a test tube as a pestle. Do not warm. The treatment should not be longer than five minutes before filtering off the solution. Wash any black residue. †

---

* If phosphates or oxalates may be present (see page 72).

Residue: CoS, NiS	Filtrate: $FeCl_2$, $AlCl_3$, $CrCl_3$, $MnCl_2$, $ZnCl_2$			
Test with borax bead (see Experiment 19 (1) (p. 58). If cobalt is present, test for Ni as follows: Dissolve precipitate in 1 or 2 cc. of aqua regia, evaporate almost to dryness, take up in a little water, add excess sodium acetate and a few drops of dimethyl glyoxime. Or, test solution for nickel according to the footnote under Experiment 20 (p. 58).	Boil to drive off H_2S, place in an evaporating dish, make alkaline with NaOH*, and add about 1 g. Na_2O_2 to cold solution. Boil until *all* the peroxide is decomposed. Filter quickly. Why? Wash.			
	Precipitate: $Fe(OH)_3, MnO(OH)_2$ Dissolve in dilute H_2SO_4 and divide into two parts. Test one part for Fe by KCNS, and the other for Mn by lead-dioxide test (p. 58).	**Filtrate** Contains $NaAlO_2$, Na_2ZnO_2, Na_2CrO_4. Neutralize at once with HNO_3. then make alkaline with NH_4OH. White precipitate shows Al. Filter.		
		Precipitate: $Al(OH)_3$ Confirm the presence of aluminium by treating the white precipitate as described in Experiment 16 (1) (p. 55).	**Filtrate:** Na_2CrO_4, $Zn(NH_3)_4(OH)_2$ Acidify with acetic acid and divide into two parts: (a) and (b).	
			(a) Add lead acetate; a yellow precipitate is lead chromate.	(b) Add barium chloride; a light yellow precipitate is barium chromate. Filter.
			Precipitate: $BaCrO_4$	**Filtrate †** Warm the acetic acid solution and saturate with hydrogen sulfide. A white precipitate is obtained if zinc is present. Confirm by Experiment 16 (2) (p. 55).

* If Mn is not found, add to this filtrate a few drops of $Mn(NO_3)_2$ and boil to decompose completely any peroxide which may have remained in the solution. If this is not done the test for zinc may be interfered with by the precipitation of sulfur.

† Sometimes it is better to let the tube just touch the surface of the solution and pass in only a little H_2S while shaking.

Experiment 18

To two or three drops of manganese sulfate solution add 5 cc. of dilute sulfuric acid and enough lead dioxide to fill the rounded bottom of the test tube. Boil for a minute or two and allow the suspended material to settle. Note the color of the solution and explain. Chlorides *must not* be present in making this test for manganese. Why?

Experiment 19

1. Bend a platinum wire around the point of a lead pencil so as to make a small loop. Heat the loop to redness, dip it into a little borax, and then fuse the portion sticking to the wire into a clear bead. While the bead is still hot touch it to a *very small* particle of cobalt salt and then heat strongly in the oxidizing flame. Cool, and note the color of the bead. Repeat this experiment, using a nickel salt and a manganese salt instead of the cobalt.

2. Make a bead as described in 1, using sodium carbonate to which is added a small particle of potassium nitrate. Touch the bead to a small particle of manganese salt and fuse in the oxidizing flame. Cool, and note the color.

Experiment 20 *

Precipitate a little nickel sulfide, filter, and dissolve the precipitate in a few drops of aqua regia. Evaporate almost to dryness, stopping before the last drop has disappeared in order to avoid overheating. Add a few cubic centimeters of water, then a large excess of solid sodium acetate and a few drops of dimethyl glyoxime reagent.

Experiment 21

To a solution of zinc sulfate add sodium hydroxide until the precipitate first formed dissolves. Divide this solution into two parts. Pass hydrogen sulfide into one part. Acidify the other part with acetic acid and pass in hydrogen sulfide. Explain.

* Mix together one volume of a cobalt chloride solution with one-half volume of nickel chloride. Add to this mixture an excess of sodium potassium tartrate and of sodium hydroxide. Saturate the solution completely with hydrogen sulfide. Filter, and note the very dark-brown-colored filtrate. What is the precipitate? What causes the color in the filtrate?

THE COPPER GROUP

The ions to be tested for in this group are Hg^{++}, Pb^{++}, Cu^{++}, Bi^{+++}, and Cd^{++}.

Mercury, copper, and cadmium are marked by their tendency to form complex ions with ammonia or potassium cyanide (see page 50), while lead is amphoteric (see page 49), forming both lead salts and plumbites, the alkali salt of the latter being soluble. Lead also is interesting in that it forms an insoluble sulfate. Mercury and cadmium are unusual in that their salts, particularly the chlorides, are very slightly ionized, and this ionization may be still further decreased by the addition of a common negative ion. Advantage is sometimes taken of this in the separation of cadmium from copper. Copper forms two series of compounds, cuprous (Cu^+) and cupric (Cu^{++}), but the former are so easily oxidized to the latter that they are never used for identification. Most cupric salts are highly colored and can be easily identified by this means. Like copper, mercury forms two series of compounds, mercurous (Hg^+) and mercuric (Hg^{++}). The mercurous ion, forming an insoluble chloride, is always tested for in the silver group. As mercurous salts oxidize easily to mercuric, the latter will nearly always be present if the mercurous ion has been found in the silver group. Mercuric salts are rather easily reduced to mercurous or even to free mercury by strong reducing agents, such as stannous chloride, and this property is often used for their identification.

Bismuth, although it occurs in the fifth group of the periodic table, behaves mostly as a metal and shows few unusual reactions, except that its salts are considerably hydrolyzed. The products of hydrolysis are mostly insoluble basic salts, one of the least soluble and most characteristic being the oxychloride ($BiOCl$). The reaction is easily reversed and the salt dissolves again in an excess of acid.

Experiment 22

1. Acidify a solution of mercuric chloride with dilute hydrochloric acid, heat to boiling, and saturate with hydrogen sulfide. Filter, and test the solubility of the precipitate in boiling dilute nitric acid. Keep the volume of acid constant during boiling.

2. Repeat 1, using 3–5 cc. of each of the following solutions : lead acetate, bismuth chloride, copper sulfate, and cadmium sulfate.

Experiment 23

1. Using solutions of lead acetate, bismuth chloride, copper sulfate, and cadmium sulfate, add to each one drop of ammonium hydroxide, shake, and then add an excess.

2. Filter off the precipitate formed in the bismuth chloride and wash the precipitate into the tip of the filter with a little warm water. Now pour a few drops of dilute hydrochloric acid on the precipitate in the filter and allow one to two drops to fall into a beaker containing at least 100 cc. of cold water.

Experiment 24

Add dilute sulfuric acid to a solution of lead acetate. Filter, and wash the precipitate. Dissolve in sodium hydroxide, acidify the solution with acetic acid, and then add potassium dichromate.

Experiment 25

Mix together a few cubic centimeters of copper sulfate and cadmium sulfate. Acidify 3 cc. of the mixture with hydrochloric acid and add solid sodium chloride until the solution is saturated. Warm the solution and saturate it with hydrogen sulfide. Filter through a *dry* filter paper. Dilute the filtrate with several times its volume of water and again saturate it with hydrogen sulfide.

Experiment 26

Acidify a solution of copper sulfate with 5 cc. of concentrated nitric acid. Warm and pass in hydrogen sulfide for two or three minutes. Recall that HNO_3 is a strong oxidizing agent and account for the brown vapors and the yellowish precipitate which forms. *Nitric acid should always be avoided when precipitating with hydrogen sulfide.* How could it be removed if present ?

SCHEME FOR ANALYSIS OF THE COPPER GROUP

The solution is acidified with HCl until the methyl-violet test (see Experiment 13) shows it to be about .25 molar, warmed, and saturated with H_2S. A small portion is filtered and the filtrate tested with H_2S to insure complete precipitation. When precipitation is complete, filter, wash with hot water, and transfer the precipitated sulfides to an evaporating dish. Add 10 cc. dilute HNO_3 and grind up the precipitate, using a test tube as a pestle. Boil, keeping the volume of the liquid constant during boiling. Filter, and wash any residue with hot water. The residue may be merely sulfur, in which case it may be discarded, or it may be mercury sulfide. This may be in the form of black HgS or heavy yellow or whitish $Hg(NO_3)_2 \cdot 2\ HgS$.

Residue: HgS

Dissolve in aqua regia, evaporate nearly to dryness. Add 2–3 cc. of dilute HCl, and again evaporate nearly to dryness. Add water, and filter if not clear. Add $SnCl_2$. A white precipitate of $HgCl$ forms if Hg is present. If much $SnCl_2$ is added the precipitate will change to gray or black, due to formation of metallic mercury.

Filtrate: $Pb(NO_3)_2$, $Bi(NO_3)_3$, $Cu(NO_3)_2$, $Cd(NO_3)_2$

Add 2–5 cc. of dilute H_2SO_4, and evaporate the solution to about 1 cc., or until heavy white fumes are evolved. Cool and pour into 20 cc. water. Filter.

Precipitate: $PbSO_4$

Dissolve in NaOH. Acidify with $HC_2H_3O_2$ and then add $K_2Cr_2O_7$. Yellow precipitate is $PbCrO_4$.

Filtrate: $Bi_2(SO_4)_3$, $CuSO_4$, $CdSO_4$

Make solution strongly alkaline with NH_4OH. If Cu is present the solution will be blue. White precipitate *may* be $Bi(OH)_3$ and must be tested. Filter.

Precipitate: $Bi(OH)_3$

Filter off the white precipitate and test it for Bi as described in Experiment 23(2) (p. 60).

Filtrate

The solution contains the ions $Cu(NH_3)_4{}^{++}$ and $Cd(NH_3)_4{}^{++}$. Acidify with HCl, evaporate to a small volume, cool, and saturate with solid NaCl. Warm and saturate with H_2S. Filter. When all the Cu^{++} has been removed, dilute filtrate with five volumes of water and again saturate with H_2S. Yellow precipitate or coloration proves Cd.

THE ARSENIC GROUP

The ions to be tested for in this group are As^{+++}, As^{+++++}, Sb^{+++}, Sb^{+++++}, Sn^{++}, and Sn^{++++}.

The fact has already been mentioned that arsenic, antimony, and tin are decidedly nonmetallic, particularly in their higher valences, and that this property is taken advantage of in separating them from the metals of the copper group.

Arsenic, in its highest valence, forms a rather strong acid, arsenic acid (H_3AsO_4), similar to phosphoric acid, and any basic properties which it may show are very weak. For this reason it is usually very difficult to precipitate arsenic from arsenic solutions by means of hydrogen sulfide. Arsenious acid is a weaker acid and shows more pronounced basic properties, so that arsenic trisulfide may be precipitated without difficulty from such solutions.

Hydrogen sulfide slowly reduces arsenic acid to arsenious acid, which is then precipitated as the trisulfide along with some pentasulfide. Heat increases the rate of this reduction, and a large excess of hydrochloric acid favors the precipitation of the pentasulfide.

Arsenic acid, being very similar to phosphoric acid, easily forms such compounds as magnesium ammonium arsenate ($MgNH_4AsO_4$), this compound forming a characteristic, crystalline precipitate in strong ammoniacal solution.

Antimonic acid shows more basic properties than arsenic acid, and the pentasulfide is easily precipitated.

Antimony compounds are easily reduced by hydrogen, in the presence of metals, to metallic antimony, which appears as a fine black deposit.

Both stannous and stannic acids show some basic properties, hence stannous and stannic sulfides are precipitated without difficulty. However, these sulfides are soluble in much hydrochloric acid and can only be precipitated when

the concentration of this acid is small. Hence the necessity, frequently, of greatly diluting the solution after arsenic has been precipitated. This difference in the solubility of the sulfides of arsenic, antimony, and tin in hydrochloric acid is often taken advantage of in separating them.

Stannous salts are easily oxidized to stannic, so that stannous chloride readily reduces ferric salts to ferrous, mercuric to mercurous or free mercury, and molybdic acid to lower oxides of molybdenum.

SCHEME FOR ANALYSIS OF THE ARSENIC GROUP

The solution containing compounds of arsenic, antimony, and tin is acidified with about 2 cc. of concentrated HCl warmed and saturated with H_2S. Now dilute until the acidity is .25 molar and again saturate with H_2S. Filter, and wash the precipitate with hot water. Transfer the precipitated sulfides to an evaporating dish and add to them 3 or 4 cc. of concentrated hydrochloric acid. Care must be taken not to dilute the acid in any way. Grind up the precipitate with the acid and warm the mixture as long as there is a brisk evolution of hydrogen sulfide. Cool and filter through a *dry* filter. Saturate the filtrate with hydrogen sulfide. If a yellow precipitate of arsenic sulfide forms, it must be filtered out of the solution.

Residue: As_2S_3, As_2S_5	Filtrate: $SbCl_3$, $SnCl_4$, $SnCl_2$
Dissolve the precipitate in concentrated HCl containing a few crystals of potassium chlorate and test with NH_4OH and $MgCl_2$ (see Experiment 28, p. 64).	Boil until the hydrogen sulfide is entirely removed from the filtrate, which should then have a volume of 2 cc. Dilute with an equal volume of water and test for antimony and tin as described in Experiment 29, p. 64, by adding nails etc.

Experiment 27

Take solutions of sodium arsenite, of antimony chloride, and of stannous chloride and add to each about 1 cc. of dilute hydrochloric acid. Warm each solution and saturate with hydrogen sulfide. Test the solubilty of each precipitate in concentrated hydrochloric acid. To the solutions of the precipitates which have dissolved add water, drop by drop, until the precipitate reappears. Note approximately the amount of water added before each precipitate reappears.

Experiment 28

Precipitate some arsenic sulfide and dissolve it in concentrated hydrochloric acid to which a few crystals of potassium chlorate have been added. Evaporate nearly to dryness, add a small amount of water, an excess of ammonium hydroxide, and some magnesium chloride solution. The precipitate may not form immediately. If not, shake vigorously and let stand.

Experiment 29

Mix together a few cubic centimeters of antimony chloride and stannous chloride. Add a few drops of HCl and several small iron tacks or nails to the solution and heat to boiling for two or three minutes. A vigorous evolution of hydrogen will occur and a dark granular deposit appear. Filter, and treat the residue and filtrate as follows : Dissolve the residue in about 5 cc. of hot tartaric acid solution containing three or four drops of dilute nitric acid. Place in a precipitation flask and pass in hydrogen sulfide, preferably keeping the delivery tube just above the liquid. Shake the solution. Divide the filtrate from the granular residue into two parts. To one part add a little mercuric chloride solution. Dilute the other part with 30–50 volumes of water and add 2–3 cc. of a neutral ammonium molybdate solution.

SCHEME FOR SEPARATION OF THE ARSENIC AND COPPER GROUPS

The solution, which may contain metals of both groups, should be clear. It is acidified rather strongly with HCl, warmed, then saturated with H_2S as long as any precipitate forms. Filter, dilute the filtrate until the acidity is approximately .25 molar, and again saturate with H_2S. Filter through the same filter and test the filtrate by passing in more H_2S. Wash the precipitate two or three times with hot water.

Precipitate: HgS, PbS, Bi_2S_3, CuS, CdS, As_2S_3, As_2S_5, Sb_2S_3, Sb_2S_5, SnS, SnS_2	Filtrate
Transfer a small portion of the precipitate to a test tube, add 1 cc. $(NH_4)_2S_x$, and warm to about 60°. Filter, and test the filtrate for members of arsenic group by acidifying with HCl. If only a white or yellowish precipitate of sulfur is thrown down, the arsenic group is not present, but if a yellow, orange, or brown flocculent precipitate is obtained, the arsenic group is present. If the arsenic group is present, transfer the whole precipitate obtained by H_2S to a beaker or evaporating dish and treat with $(NH_4)_2S_x$, as directed above. Filter. Wash.	Contains iron-zinc and other groups, and is set aside to be tested for them later (see page 56).

Filtrate: $(NH_4)_3AsS_4$, $(NH_4)_3SbS_4$, $(NH_4)_2SnS_3$	Residue
Acidify filtrate. Filter, wash, transfer to an evaporating dish and analyze the precipitate according to scheme for analysis of arsenic group, beginning where the precipitate is ground with 3 or 4 cc. of HCl (p. 63).	Sulfides of the copper group. To be analyzed according to scheme for analysis of copper group, beginning by dissolving the precipitate in dilute HNO_3 (p. 61).

THE SILVER GROUP

This group includes silver, lead, and mercurous mercury. Silver forms but one series of salts, and in this it is univalent. Mercury forms two series of salts. In the mercuric salts it has a valence of two, while in the mercurous salts it has a valence of one. Lead most commonly shows a valence of two. It is, however, tetravalent in some of its compounds, and also occurs in the acid ions PbO_3^{--}, PbO_4^{----}.

Silver and mercury have a marked tendency to enter into complex ions, as $KAg(CN)_2$, $Ag(NH_3)_2Cl$, NH_2HgCl, while lead behaves in a more normal manner. The formation of these complex ions plays an important part in the separation and identification of these elements.
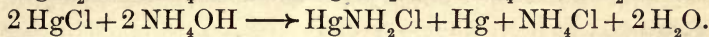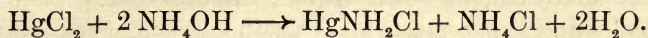
The chlorides of silver and mercurous mercury are very difficultly soluble in water. Lead chloride is only sparingly soluble in cold water, but is soluble in hot water. One hundred cubic centimeters of water will dissolve about 1.1 grams of $PbCl_2$, 0.000038 grams of $HgCl$, and 0.00015 grams of $AgCl$ at ordinary temperatures. At $100°$ the same amount of water will dissolve about 3.5 grams of $PbCl_2$.

As a group precipitant hydrochloric acid will be used. This will precipitate silver and mercurous mercury almost completely, but will leave some of the lead in solution. If the solution is very dilute with respect to lead, no precipitate of lead may be thrown down by hydrochloric acid, but will be precipitated with the copper-arsenic groups as sulfide and can be identified there. Lead should always be tested for in the copper group, whether it is found in the silver group or not. Mercuric mercury will be precipitated as sulfide with the copper arsenic groups.

Silver chloride dissolves in ammonium hydroxide, forming the soluble complex salt $Ag(NH_3)_2Cl$. This compound gives so few silver ions that a chloride will cause no precipitate in

neutral or alkaline solution. If the solution is acidified the complex ammonia ion will be broken up and the silver chloride reprecipitated.

Mercuric and mercurous chlorides interact with ammonium hydroxide to form the white insoluble compound $HgNH_2Cl$.

$$HgCl_2 + 2\,NH_4OH \longrightarrow HgNH_2Cl + NH_4Cl + 2H_2O.$$
$$2\,HgCl + 2\,NH_4OH \longrightarrow HgNH_2Cl + Hg + NH_4Cl + 2\,H_2O.$$

The mercurous compound gives a black coloration, due to the formation of metallic mercury.

Lead forms an insoluble chromate $PbCrO_4$, which is soluble in strong alkalies, with the formation of a compound with the $PbO_2{}^{--}$ ion. This shows the amphoteric character of lead hydroxide.

Bromine acts as an oxidizing agent, oxidizing mercurous compounds to mercuric compounds.

As mercurous compounds are so easily oxidized to mercuric compounds, if the former are found the latter will nearly always be present, and will be identified in the copper group.

Experiment 30

Use solutions of the nitrates of silver, lead, and mercurous mercury. To each solution add hydrochloric acid. Bring the precipitated chlorides on filters, and wash once with cold water. Treat each precipitate with about 50 cc. of hot water in portions of about 10 cc. at a time. Divide the solution from the precipitate which dissolves into two parts. To one part add potassium dichromate solution and to the other dilute sulfuric acid. Add sodium hydroxide to the precipitated chromate and then acidify with acetic acid.

To the two precipitates which did not dissolve in hot water add 1 cc. of ammonium hydroxide, catching what runs through in clean test tubes. Make the solution in each test tube acid with dilute nitric acid. Treat the black residue with a saturated solution of bromine water.

Experiment 31

Add stannous chloride to solutions of mercuric and mercurous salts. Stannous chloride acts as a reducing agent, being itself oxidized to stannic compounds.

Experiment 32

Heat silver chloride with sodium carbonate on a piece of charcoal with the blowpipe. Repeat with lead and mercury salts.

Experiment 33

Expose silver chloride to sunlight for a short time.

SCHEME FOR ANALYSIS OF THE SILVER GROUP

Solution contains silver, lead, and mercurous mercury. Acidify with HNO_3. Add HCl until precipitation is complete. Filter, and wash precipitate with cold water.

Precipitate: $AgCl$, $PbCl_2$, $HgCl$

Wash the precipitate on the filter with 5 cc. of hot water, catching the water in a test tube, and divide into two parts. Test for lead by adding to one part a few drops of H_2SO_4 and to the other $K_2Cr_2O_7$ solution. If lead is found, continue washing with hot water until the last portion of the wash water gives no precipitate with H_2SO_4.

Residue: $AgCl$, $HgCl$		Filtrate: $PbCl_2$
Treat with warm ammonium hydroxide.		Add acetic acid and potassium chromate. A yellow precipitate of $PbCrO_4$ shows the presence of lead. This may be confirmed by dissolving in sodium hydroxide and reprecipitating with acetic acid.
Black Residue: $HgNH_2Cl + Hg$ Shows the presence of mercury.	**Filtrate: $Ag(NH_3)_2Cl$** Acidify with HNO_3. White curdy precipitate shows the presence of silver.	

If a large amount of mercurous chloride and a small amount of silver chloride is present, ammonium hydroxide may fail to dissolve the silver chloride. If no test for silver is obtained and mercury is present, wash the black residue repeatedly with hydrochloric acid and saturated bromine water. Wash the residue with hot water and repeat treatment with ammonium hydroxide and nitric acid.

ANALYSIS FOR ACID IONS

In the systematic analysis for metal ions these ions are divided into very definite groups, and in general the ions of any one group are tested for in the absence of all other groups.

Acid ions also are usually divided into groups, but this grouping shows considerable variation, depending upon the method of analysis used. The grouping generally depends upon the behavior of the ions with certain reagents, such as barium chloride and silver nitrate, either in acid or neutral solution. As a rule the groups are not separated from each other for analysis. In an analysis for the acid ions two general plans may be followed. In one the metal ions, other than those of the alkali metals, are removed before testing for the acid ions, and the tests frequently made in neutral or alkaline solution. If these ions were not removed many of the tests would be interfered with by them. For example, in testing for a nitrate, if barium were present the addition of ferrous sulfate would produce a precipitate of barium sulfate which would interfere more or less with the test. In the other plan the acid ions are tested for in acid solution, and metal ions as a rule do not interfere. In this outline so few acid ions will be studied that no grouping will be attempted, but each acid will be identified by a special test. The method in which the metal ions other than the alkali metal ions are removed will be used.

It must be remembered that usually few acid ions will be found in any mixture. Much information can often be gained as to the acid ions which may be present or absent in a mixture or compound by observing the solubility of the substance in water and acids when the nature of the metal ions is known. For example, the sulfate ion and barium ion could not both be present in an unknown which is soluble in water or dilute acids.

The acid ions to be studied in this outline are chloride (Cl^-), nitrate (NO_3^-), sulfate (SO_4^{--}), phosphate (PO_4^{---}), carbonate (CO_3^{--}), acetate ($C_2H_3O_2^-$), tartrate ($C_4H_4O_6^{--}$), and borate (BO_3^{---}).

PREPARATION OF THE SOLUTION

If the unknown contains cations higher than the alkali group, these must be removed before testing for anions. To do this mix some of the original with water (complete solution is not necessary), boil, and to the hot solution add saturated Na_2CO_3 solution so long as a precipitate is formed. Boil for a few minutes. This precipitates as carbonates the metals which might interfere. Filter and test for NO_3^-, Cl^-, SO_4^{--}, and PO_4^{---} ions in separate portions of this solution. *Each portion to be used in making a test must be acidified as directed in the preliminary experiments.* The CO_3^{--}, $C_2H_3O_2^-$, and $C_4H_4O_6^{--}$ ions may be tested for in separate portions of the original unknown.

If phosphate or tartrate ions are found, these must be re-moved before testing for certain of the cations. For special separation in case of the presence of phosphate ion, see page 72.

In case tartrate is found, this is decomposed before testing for any cations by treating the original with concentrated H_2SO_4 and evaporating to dryness. Repeat until there is no odor of tartrate. The residue is then used for tests for cations in the usual way.

TESTS FOR ANIONS (SO-CALLED ACIDS)

PRELIMINARY TESTS

Chloride (Cl^-). Add to a solution of hydrochloric acid a few drops of a silver nitrate solution. Test the solubility of the precipitate in dilute nitric acid, and in ammonium hydroxide. After dissolving the precipitate in ammonium hydroxide acidify the solution with nitric acid.

Nitrate (NO_3^-). Add to a solution of potassium or sodium nitrate about one half its volume of freshly prepared ferrous sulfate solution, which has been acidified with dilute sulfuric acid, and mix the two solutions. Incline the test tube and carefully pour down the side of the tube a small quantity of concentrated sulfuric acid, being careful not to mix the two liquids more than necessary. The mixture must be kept cool. What forms at the juncture of the two liquids?

Sulfate (SO_4^{--}). To a solution of potassium or sodium sulfate, previously acidified with HNO_3 or HCl, add barium chloride solution.

Phosphate (PO_4^{---}). Acidify a few drops of a solution of a soluble phosphate with nitric acid. Add an excess of ammonium molybdate solution, and warm.

Carbonate (CO_3^{--}). Carbonates when treated with acids effervesce, due to the evolution of carbon dioxide, a colorless, odorless, noncombustible gas. Treat a carbonate with a dilute acid and pass the gas formed into lime water.

Acetate ($C_2H_3O_2^-$). Add to sodium acetate a little sulfuric acid (1:1), warm, and note the odor. To another portion add alcohol and sulfuric acid, warm, and note odor. The odor in the first case is due to acetic acid, and in the latter to ethyl acetate ($CH_3COOC_2H_5$).

Tartrate ($C_4H_4O_6^{--}$). Heat a small amount of solid sodium tartrate or sodium potassium tartrate on a crucible lid. Note the odor of burnt sugar. The test is made more conclusive by first moistening the tartrate with concentrated sulfuric acid and then heating.

Borate (BO_3^{---}). Evaporate just to dryness the solution to be tested. Add about 5 cc. of methyl alcohol and 2 cc. of concentrated sulfuric acid and stir the mixture. If the alcohol is now ignited, the flame will be green-bordered. The color is due to the formation of methyl borate (($CH_3)_3BO_3$), which is volatile and imparts a green color to the alcohol flame. The alcohol may be ignited in an evaporating dish, or, better, put into a test tube fitted with a one-hole stopper carrying a glass tip. The mixture in the test tube is heated and the alcohol ignited as it issues from the tip.

Special Method for the Separation and Identification of Metal Ions of the Iron-Zinc Group in the Presence of Phosphate or Oxalate Ions

As the phosphates of metals above the alkali group are insoluble in water, if the phosphate ion is present phosphates of the metals of the iron-zinc and alkaline earth groups will be precipitated when the solution is made alkaline with ammonium hydroxide before the iron-zinc group is precipitated with hydrogen sulfide (see page 56). Hence, if the phosphate ion has been found, it is necessary to use a special method for the separation of these two groups. Tests should always be made for the phosphate ion before the iron-zinc group is precipitated. If it is found, the filtrate from the copper group is boiled with about 10 cc. of bromine water to oxidize the iron and a small portion of this solution tested for iron by the usual reagents (see page 56). Neutralize the remainder of the solution with ammonium hydroxide and acidify strongly with acetic acid. Add 5 cc. of a 50 per cent ammonium-acetate solution and, if the solution is not reddish-brown in color, add ferric chloride solution, drop by drop, until this color is produced. Boil the solution, diluting with water during boiling if necessary. As ferric phosphate is the least soluble of any of the phosphates of this group, this procedure precipitates all of the phosphate ion as ferric

phosphate, with possibly some phosphates of aluminium and chromium, while the other metals remain in solution. Filter, and test the filtrate by addition of more ammonium acetate and boil. Continue this treatment as long as any ferric phosphate is precipitated. When all the phosphate has been removed, the solution is treated by the usual method for the separation and identification of the iron-zinc, alkaline earth, and alkali groups. If desired the precipitate may be tested for aluminium and chromium by the usual treatment with sodium peroxide.

Method of Procedure with an Unknown Substance

The substance will be a liquid or a solid (gases will not be considered in this outline), and may be either a single substance or a mixture.

It should first be examined for the usual physical properties, — particularly color, taste (care!), odor, and, if it is a solid, crystalline form, solubility, etc. —, as these may give much information in regard to its nature. Heating a little of the solid on platinum foil or, if a liquid, evaporating and heating the residue will show whether or not this material is organic and give information as to the melting and volatilizing points. In the case of solids other easily performed tests, as heating in a closed tube and heating with sodium carbonate on charcoal, may frequently be used to advantage.

If the substance is a solution it should be tested with litmus, and if neutral or acid the analysis begun without further treatment. If alkaline it must be neutralized and any precipitate which forms dissolved before the analysis is begun. When solids are to be dissolved, take a *small* representative portion of the material and try dissolving it in distilled water, remembering that many substances are only moderately soluble in water. If it does not dissolve, heat the water. If there is no result, add a few drops of dilute nitric

acid, first in the cold and then with heat, gradually increasing the amount of acid necessary. If still unaffected, repeat on another portion, using hydrochloric acid instead of nitric acid. If both nitric and hydrochloric acids fail, aqua regia may be tried, but the instructor should first be consulted. When large amounts of strong acids are added, the excess of acid should be removed by evaporating before proceeding with the analysis. If the substance is only partly soluble it is sometimes convenient to analyze the solution and residue separately. Most residues insoluble in acids can be taken into solution by fusing with sodium or potassium carbonates and by subsequent treatment with acids. In extreme cases fusion with sodium hydroxide or sodium peroxide may be necessary. In the case of compounds of antimony and tin the addition of sulfur to the fusion mixture may assist.

PROCEDURE FOR ALLOYS

Take a small portion of the alloy and treat with *dilute nitric* acid with the aid of heat.

Most alloys will dissolve completely by this treatment, except those containing antimony and tin, in which case a whitish or gray residue will remain. If gold or platinum are in the alloy a metallic-looking residue will be left, while carbon, if present, will appear as a black residue. If the residue is carbon it is filtered off and discarded, while platinum and gold are dissolved in aqua regia.

The residue left from alloys containing tin and antimony consists of the oxides of these metals (SnO_2, Sb_2O_5). Treat with hot concentrated tartaric acid solutions. Filter and test the filtrate for antimony by acidifying with hydrochloric acid and precipitating with hydrogen sulfide. The residue may be boiled with concentrated hydrochloric acid and this solution tested for tin.

Another method consists in fusing the residue, of tin and antimony oxides, with sodium hydroxide (or carbonate) and sulfur, which converts the oxides into the thio salts. The fused mass is dissolved in water and acidified with hydrochloric acid, which precipitates SnS_2 and Sb_2S_5. The identification of these sulfides is then made in the usual manner (see page 63).

The nitric acid solution of the alloy is evaporated to small volume to remove excess of acid, water added, and the analysis made according to the usual outline for the identification of metal ions. In alloys it is unnecessary to test for acid ions except in rare cases, and tests for the metals of the alkaline earth and alkali groups, with the exception of magnesium, may be omitted.

PROCEDURE FOR BAKING POWDERS

The metal ions found in baking powders will be found in the iron-zinc, alkaline earth, and alkali groups. All salts should be soluble in water. The analysis is somewhat interfered with by the presence of the starch which is in the baking powder. In order to get rid of the starch, about 5 grams of the sample is stirred with 50 cc. of cold water for fifteen to twenty minutes. The starch is allowed to settle and the solution filtered. The filtrate is taken for analysis, and the metal ions and acid ions are identified in the usual way.

QUESTIONS

1. Name some physical properties frequently made use of in identifying substances.

2. Define and illustrate combination, decomposition, double decomposition, reversible reaction.

3. Distinguish between mixtures, compounds, and solutions.

4. Define and illustrate: solute, solvent, dilute solution, concentrated solution, saturated solution.

5. Define and illustrate: gram-molecule, molar solution, normal solution, tenth normal solution, strength of solution.

6. (1) Calculate the molar concentration and normality of a solution containing in 100 cc. 36 grams of NH_4Cl; 11.42 grams of $(NH_4)_2CO_3 \cdot H_2O$; 27.02 grams of $FeCl_3 \cdot 6 H_2O$; 2 grams of $CaCl_2 \cdot 6 H_2O$; 0.0003 grams of $BaCrO_4$; 5 grams of $Ba(OH)_2 \cdot 8 H_2O$; 4 grams of $(NH_4)_2C_2O_4 \cdot H_2O$; 3.58 grams of $Na_2HPO_4 \cdot 12 H_2O$; 5 grams of $K_2Cr_2O_7$; 2 grams of $BaCl_2 \cdot 2 H_2O$. (2) What volume of the $(NH_4)_2C_2O_4$ solution would be required to precipitate all the Ca^{++} ion in 5 cc. of the $CaCl_2$ solution? (3) What weight of $BaCrO_4$ would be produced by precipitating all the Ba^{++} ion in 5 cc. of the $BaCl_2$ solution? (4) What weight of $MgNH_4PO_4$ could be precipitated by using 5 cc. of the Na_2HPO_4 solution?

7. (1) Using the following data, plot the curves of solubility for NaCl, KNO_3, CaO, and $MnSO_4$. The solubility of each substance is expressed as grams in 100 grams of water.

T°C	NaCl	KNO₃	CaO	MnSO₄	T°C	NaCl	KNO₃	CaO	MnSO₄
0	35.7	13.3	0.1382	55.4	50	37.0	85.9		74.8
5	35.7	17.2		58.2	60	37.3	110.9	0.0869	65.9
10	35.8	21.1	0.1343	61.1	65	37.5	124.9		61.5
15	35.9	26.1	0.1300	63.8	80	38.4	172.0		61.5
20	36.0	31.2		66.3	90	39.1	206.0		60.3
30	36.3	44.3	0.1163	70.4	100	39.8	247.0	0.0577	52.9
40	36.6	64.0	0.1006	73.1					

(2) At what temperature would sodium chloride and potassium nitrate have the same solubility? (3) In general, what is the effect of increasing the temperature on the solubility of substances? (4) Discuss the solubility curves by applying the law of Le Chatelier.

8. The density of a gas at 740 mm. pressure and 20° is 1.7426. What is the molecular weight? Analysis of the gas gave : carbon, 27.27 per cent; oxygen, 72.73 per cent. Find the molecular formula.

9. How does the strength of a solution affect the boiling and freezing points of the solution? How does it affect the vapor pressure and osmotic pressure?

10. What is the relation between the molar concentration and the factors mentioned in question 9?

11. State Avogadro's hypothesis, and explain or illustrate it so as to show that you understand its meaning.

12. If 21.875 grams of a substance dissolved in 1000 grams of water caused a lowering of the freezing point 0.2225°, what is the molecular weight? If the substance were composed of carbon 39.54 per cent, hydrogen 7.68 per cent, and oxygen 52.78 per cent, what would be its molecular formula?

13. When 18 grams of a substance were dissolved in 200 grams of water, the solution boiled at 100.26°. What is the molecular weight?

The percentage composition was carbon, 40 per cent; hydrogen, 6.7 per cent; oxygen, 53.3 per cent. Find the molecular formula.

14. If 0.00017 grams of $BaSO_4$ dissolve in 100 cc. of water, how many liters would be required to dissolve one gram? Such a solution would be saturated ; would it be concentrated? If the barium sulfate in this solution were 100 per cent dissociated, what would be the molar concentration of the Ba^{++} ion and the solubility-product constant for $BaSO_4$?

15. A mixture of NH_4Cl, KNO_3, and Na_2SO_4 is dissolved in water. Make a list of the possible constituents in the solution.

16. What classes of substances when in solution show abnormal changes in boiling and freezing point? How are these abnormal changes explained? What regularity in double decomposition reactions is shown by these substances in solution which is not shown when they react dry?

17. Make a clear, brief statement of the ionic theory.

18. State several reasons for believing in the ionic theory.

19. What substances capable of reacting are in each of the following solutions: NaCl, NaOH, H_2SO_4, $CuSO_4$, Br_2, Na_2HPO_4.

20. How does dissociation change with dilution? Does it change in the same degree for every substance? Define strong acids and weak acids; strong bases and weak bases. Name some in each class.

21. Explain what we mean when we say that a solution in a closed vessel does not evaporate. Why does a crystal of sodium chloride put into a saturated solution of salt appear not to dissolve?

22. Define equilibrium as applied to chemical reactions. Define a reversible reaction.

23. What would be the result of adding hydrogen chloride to a saturated solution of sodium chloride? Explain.

24. State the Mass Law and illustrate by some examples.

25. Using the data given on page 5, calculate the ionization constants for HCl, $HC_2H_3O_2$, and NaCl. HCl gas is liberated from a concentrated hydrochloric acid solution by adding concentrated sulfuric acid. Explain.

26. Using the data given on page 10, calculate the molar concentration of OH^- ion in 0.1 normal KOH; Cl^- ion in 0.1 normal HCl; SO_4^{--} ion in 0.1 normal H_2SO_4; CO_3^{--} ion in 0.1 normal H_2CO_3; S^{--} ion in 0.1 normal H_2S.

27. Solid sodium acetate is added to 0.01 normal acetic acid until the solution is 0.1 normal with respect to the sodium acetate. If the original solution were 4.2 per cent ionized, and the sodium acetate solution 80 per cent, calculate the change in molar concentration of the hydrogen ion.

28. Explain by means of the Mass Law the effect of adding NH_4Cl to a solution of NH_4OH. Why would the effect not be so noticeable if NaCl was added to NaOH?

29. What effect does the addition of sodium acetate have upon the strength of a solution of acetic acid? Explain. Would the result be the same if sodium acetate was added to a solution of hydrochloric acid? Explain.

30. (1) Solid NH_4Cl is added to 0.1 molar NH_4OH solution until the solution is 0.1 molar with respect to the NH_4Cl. If the NH_4Cl is 80 per cent dissociated, and the original NH_4OH is 1.3 dissociated, what is the change in the molar concentration of the OH^- ion? (2) The solubility-product constant for $Mg(OH)_2$ is 3.4×10^{-11}. If the above NH_4OH-NH_4Cl solution were also 0.1 molar with respect to $MgSO_4$, 70 per cent dissociated, would $Mg(OH)_2$ be precipitated?

31. What are the three conditions which tend to bring reversible reactions to completion? Illustrate each by an equation.

32. Illustrate hydrolysis by an equation. Explain why sodium carbonate reacts alkaline in solution and copper sulfate reacts acid under the same circumstances.

33. Is the addition of water (or hydrogen and oxygen in the proportion to form water) oxidation or reduction or neither? Why?

34. Name some of the more common reducing agents and tell why each acts as a reducing agent.

35. Name some of the more common oxidizing agents and tell why each acts as an oxidizing agent.

36. Define oxidation and reduction in terms of gain or loss of hydrogen and oxygen; in terms of gain or loss of charges.

37. Would the following mixtures of compounds be completely soluble in water, partly soluble in water but completely soluble in acids, or only partly soluble in both water and acids: KNO_3, $ZnSO_4$, $AlCl_3$; $MnCO_3$, $Zn(NO_3)_2$, $CuSO_4$; $NaNO_3$, K_2CO_3, $(NH_4)_2SO_4$, Na_2HPO_4, $BaSO_4$, $NaCl$; $CaCO_3$, $FeCl_3$, $CdCl_2$, $Hg(NO_3)_2$; $HgCl_2$, $AsCl_3$, $Pb(NO_3)_2$, $Co(NO_3)_2$; $Ba(NO_3)_2$, $AgNO_3$, $Pb(NO_3)_2$, KNO_3; $Ca_3(PO_4)_2$, $MnCl_2$, $NaNO_3$?

38. Write a list of the elements to be studied in each group, and give group precipitant for each. Why is there no group precipitant for the alkali group?

39. Why must sodium hydroxide be added before heating in testing for ammonium? Why cannot the litmus paper be put directly into the solution in making the test?

40. Why must the solution be evaporated to complete dryness and heated strongly before testing for potassium with sodium cobaltinitrite? Is this procedure necessary when testing for potassium by the flame test? Why?

41. Why are ammonium salts so generally used as reagents when sodium and potassium salts are equally soluble?

42. Could ammonium be tested for in the original solution containing all the other metals? Why would it be advisable to test for it here?

43. Why do we usually use a hydrochloric acid solution or moisten the residue with hydrochloric acid before testing in the flame?

44. An unknown of the alkali group is known to contain only one metal. What is the first test you would apply? Would this test identify your metal?

45. In an alkali group unknown, if you had proved the presence of ammonium and had forgotten to evaporate and ignite before precipitating

with sodium cobaltinitrite, how could you test the precipitate to prove whether potassium is present or not?

46. Why is ammonium chloride added before precipitating the alkaline earth group? What element would be difficult to identify if the ammonium chloride had not been added?

47. Could you identify magnesium in the filtrate from the alkaline earth group by precipitating it with ammonium hydroxide? Why?

48. What is the group reagent for the alkaline earth group? Why do we not use sodium carbonate?

49. Why do we use acetic acid to dissolve the precipitated carbonates of the alkaline earth group instead of hydrochloric or some other strong acid?

50. The table on page 32 shows that $SrCrO_4$ is quite insoluble. Why is it that barium can be separated from strontium by means of the chromate ion? If the chromate ion had been added in a neutral solution what would have been the result?

51. Apply the Mass Law to the questions asked in 50.

52. (1) Use the molar solubilities given on page 32. A saturated solution of BaC_2O_4 is about 86 per cent ionized; SrC_2O_4, 89 per cent; CaC_2O_4, 96 per cent; MgC_2O_4, 33 per cent. Calculate the solubility-product constant for each of these substances. (2) If 0.1 molar sodium oxalate were 70 per cent ionized, what would be the least concentration of calcium ion which could be detected in such a solution? (3) Would the concentration of calcium ion in a saturated solution of $CaSO_4$, 53 per cent ionized, be sufficient to give a precipitate of CaC_2O_4? (4) Show from the data above whether the oxalate test for calcium could be used if barium, strontium, or magnesium ions were present.

53. Why is strontium tested for by calcium sulfate and not by sulfuric acid? Could potassium sulfate have been used under any circumstances? Explain. Apply the Mass Law to your answers.

54. Why should ammonium carbonate and ammonium oxalate be added to the filtrate from the alkaline earth group and the solution filtered before testing for magnesium?

55. If strontium is not completely removed, how and why may it interfere with the test for calcium?

56. If strontium is known to be absent, how may the separation of the alkaline earth elements be shortened? How may it be shortened if barium is known to be absent?

57. Why could we not separate the alkaline earth metals from each other as carbonates?

58. If a solution which might contain alkaline earth and alkali metals gives no precipitate for an alkaline earth metal with $(NH_4)_2CO_3$, would you evaporate to dryness and proceed at once to test for the alkali metal? Why?

59. If barium and strontium were both known to be absent, could you test the solution containing alkaline earth and alkali metals directly with $(NH_4)_2C_2O_4$ for calcium? Why?

60. What metals of the alkaline earth group can be tested for by the flame test? If a solution contained only alkaline earth and alkali metals, would the flame test alone be sufficient? What metals might still be in doubt? Could you certainly identify calcium or strontium alone or in the presence of each other by the flame test?

61. Would a green flame always be positive evidence of barium? What other substances might cause a green flame?

62. List the elements which are precipitated by hydrogen sulfide, giving the color of each precipitate. Which are soluble in dilute acids? Which are soluble in ammonium sulfide? Which are hydrolyzed and precipitated as hydroxides?

63. In precipitating with hydrogen sulfide how may we be sure that the precipitating agent always has the same concentration? What is this concentration? Would you call it a concentrated or a dilute solution?

64. Hydrogen sulfide is a dibasic acid, the principal ionization being $H^+ + HS^-$. Why do we usually find normal sulfides precipitated and not acid sulfides? Why are a few metals precipitated as hydroxides and not as sulfides by H_2S?

65. If hydrogen sulfide is passed into a neutral solution containing chlorides of all the metals of the copper-arsenic and iron-zinc groups, which sulfides would be completely precipitated, which ones only partially precipitated, and which ones would not be precipitated at all? Which sulfides would probably precipitate first? Explain.

66. Why must the solution be made distinctly acid before precipitating the copper-arsenic group with hydrogen sulfide? What would be the result if too much acid is used? if too little acid is used?

67. Why can neither nitric acid nor sulfuric acid be used to acidify the solution before precipitating the copper-arsenic group with hydrogen sulfide? What acid is best to use?

68. Explain why arsenic sulfide may be separated from bismuth sulfide by means of ammonium sulfide when they both occur in the same group of the periodic table. Why does stannous sulfide require yellow

ammonium sulfide to dissolve it, while stannic sulfide is dissolved by colorless ammonium sulfide?

69. Why do we obtain the sulfides of the metals when the ammonium sulfide solution of arsenic, antimony, and tin sulfides is treated with a dilute acid?

70. Write equations for all the reactions included in questions 68 and 69.

71. Why is it that cobalt and nickel sulfides do not precipitate with the copper-arsenic group when hydrogen sulfide is passed into the acid solution, and yet can be separated from other members of the iron-zinc group by treatment of the sulfides with hydrochloric acid?

72. Explain by the Mass Law why some sulfides are soluble in hydrochloric acid and others are not.

73. (1) Using the solubility-product table on pages 42 and 43, calculate in grams per liter the weight of mercuric ion (Hg^{++}) necessary to produce a precipitate of mercuric sulfide when the molar concentration of hydrochloric acid present is 0.2. (2) Calculate in grams per liter the weight of lead ion (Pb^{++}) necessary to produce a precipitate of lead sulfide in the same solution. (3) In what way would an increase in pressure of the hydrogen sulfide in the precipitation flask affect the precipitation of metals as sulfides? Why?

74. (1) What volume of hydrogen sulfide at 20° and 740 mm. pressure would be required to precipitate completely the cadmium in 25 cc. of a 0.2 molar solution of cadmium sulfate? (2) What weight of iron sulfide and what volume of hydrochloric acid, 7.29 per cent HCl, specific gravity 1.036, would be required to prepare this volume of hydrogen sulfide?

75. Explain why aluminium hydroxide is precipitated from a solution of an aluminium salt by ammonium hydroxide, but when sodium hydroxide is added under similar conditions the precipitate first formed dissolves.

76. Explain why zinc hydroxide is easily soluble in either dilute hydrochloric acid or strong sodium hydroxide.

77. Explain why zinc hydroxide is completely soluble in an excess of ammonium hydroxide, while aluminium hydroxide is not soluble under the same conditions.

78. Supposing an excess of sodium hydroxide were added to a solution containing all the metals of the iron-zinc group; of what would the precipitate consist? Which metals would remain in solution?

79. Suppose in question 78 ammonium hydroxide had been added instead of sodium hydroxide. Which metals would have been precipitated

and which would have remained in solution? Could this be used as a means of separation?

80. What metals are affected, and in what manner, when excess of sodium peroxide is added to a solution containing metals of the iron-zinc group?

81. If ammonium sulfide produces a black precipitate when added to a solution containing the metals of the iron-zinc group, what metals might be present? If the precipitate is light-colored what metals might be present?

82. If the ammonium sulfide precipitate of the iron-zinc group is light-colored, how may the separation be shortened? Outline the method.

83. If the ammonium sulfide precipitate is pure white, how would you proceed with the analysis?

84. Given a solution known to contain iron and zinc only, show how you would separate and identify these two elements.

85. Given a solution known to contain cobalt, chromium, and aluminium, show how you would separate and identify each of these elements.

86. On treating the dissolved sulfides of the iron-zinc group with sodium peroxide a dark-brown precipitate and a yellow solution are obtained. What two metals are probably present?

87. Why is it necessary to be careful to decompose all the hydrogen peroxide before testing for zinc? If in the final test for zinc a white precipitate insoluble in hydrochloric acid is obtained, would you report zinc? The precipitate probably is what?

88. If a phosphate is known to be present in a solution, how would you modify the analysis for the iron-zinc group?

89. What metals of the iron-zinc group can be identified by the blowpipe or borax-bead tests?

90. If a precipitate of iron, aluminium, and chromium is fused with sodium carbonate and potassium nitrate, how would you complete the analysis?

91. If the filtrate from your hydrogen sulfide precipitate of the iron-zinc group is colored pink, what is probably the trouble? How would you proceed with the analysis?

92. If the solution formed by treating the precipitated sulfides of the iron-zinc group with dilute hydrochloric acid is colored pink, to what is the color probably due, and what caused this condition? What difficulties might it cause in your analysis?

93. If when testing for chromium with lead acetate a white precipitate is obtained, does it show the presence of chromium? What is

the precipitate probably? How would you prove the presence or absence of chromium?

94. Why is the filtrate from the iron-zinc group sometimes colored brown? How may this filtrate be cleared?

95. If on making the filtrate from the copper-arsenic group alkaline with ammonium hydroxide a black precipitate is obtained, what does it indicate? What would you do?

96. If the copper-arsenic group were not completely removed by hydrogen sulfide, what difficulties would it cause in the analysis, and where?

97. What reaction takes place when borax is heated in a flame? What reaction when a metallic oxide is added to this product?

98. What is the first thing you would do if given an unknown solution for the copper-arsenic group? Why?

99. Suppose on adding hydrochloric acid to an unknown solution for the copper-arsenic group a white precipitate formed, what conclusions would you draw? How would you proceed with the analysis?

100. If on passing hydrogen sulfide into a solution of the copper-arsenic group brown vapors are observed, and the precipitate formed disappears, or does not increase, what conclusions do you draw? How would you proceed with the analysis?

101. If free nitric acid or much nitrates are present in a copper-arsenic unknown, what is the result when hydrogen sulfide is passed into the solution? What difficulties will this cause in the analysis?

102. What would be the result in precipitating the copper-arsenic group if too little hydrochloric acid is present? if too much hydrochloric acid is present? What would you do in each case?

103. If lead has been identified in the silver group, why should it be tested for and separated in the copper-arsenic group?

104. If a copper-arsenic-group unknown solution should be treated directly with nitric acid instead of first precipitating it with hydrogen sulfide, and the solution then treated with sulfuric acid and ammonium hydroxide, what element would you not have separated and how would it interfere with the analysis?

105. If mercury has been identified in the silver group, why should it be tested for and separated in the copper-arsenic group?

106. Suppose colorless ammonium sulfide had been used to separate the arsenic group from the copper group, what element might there be trouble in identifying? Explain.

107. If a black precipitate is obtained by passing hydrogen sulfide

into a copper-arsenic unknown solution, what metals might be present? If the precipitate is yellow or orange yellow, what metals might be present?

108. Suppose hydrogen sulfide produces a yellow precipitate in a copper-arsenic unknown, how may the usual analysis be shortened?

109. If the precipitate obtained in question 108 is completely soluble in yellow ammonium sulfide, how may the analysis be shortened? If entirely insoluble in yellow ammonium sulfide how may the analysis be shortened?

110. If the filtrate from the hydrogen-sulfide precipitate of the copper-arsenic group is blue, what do you suspect? What would you do?

111. If a bright-yellow precipitate should be obtained when the filtrate from the copper-arsenic group is made alkaline with ammonium hydroxide and hydrogen sulfide added, what would it signify? What would you do?

112. If sodium hydroxide is added instead of ammonium hydroxide in separating bismuth, what other elements might be precipitated? How would this affect the rest of the analysis?

113. Give two ways to distinguish between ferric and ferrous salts; to distinguish between stannic and stannous salts.

114. A solution containing ferric chloride, potassium dichromate, and aluminium chloride is made acid with hydrochloric acid and hydrogen sulfide passed into it. What is formed? Give reactions to show this.

115. Sodium hydroxide is added in excess to a solution containing ferric chloride, potassium dichromate, and aluminium chloride. What is formed? Give reactions.

116. Write equations showing the oxidation of ferrous sulfate to ferric sulfate by means of nitric acid; the reduction of ferric sulfate to ferrous sulfate by hydrogen sulfide.

117. If you should forget to treat the nitric-acid solution of the sulfides of the copper-arsenic group with sulfuric acid, but proceed at once to the addition of ammonium hydroxide, what effect would it have on the analysis? How would you complete the analysis?

118. Explain why copper and cadmium are not precipitated with bismuth by the addition of ammonium hydroxide. Why is the solution saturated with sodium chloride before copper is separated from cadmium by hydrogen sulfide? Why is the cadmium precipitated on diluting the solution after filtering off the copper sulfide?

119. Explain why we must use concentrated hydrochloric acid in separating arsenic from antimony and tin.

120. Sometimes the precipitated sulfides from the yellow ammonium sulfide solution are dark-colored. What is the cause of this? How may it be prevented?

121. How may the white precipitates of bismuth oxychloride and antimony oxychloride be distinguished?

122. After dissolving mercuric sulfide in aqua regia why is it necessary to evaporate almost to dryness and take up with water before testing for mercury with stannous chloride?

123. Why is it that mercury and lead are placed in both the silver and the copper-arsenic groups while silver, which forms an insoluble precipitate with hydrogen sulfide, is placed only in the former group?

124. In making the final test for bismuth, why is it necessary to dissolve the hydroxide in the least possible amount of acid and pour it into a large volume of water?

125. If metallic copper were placed in a solution containing all the metals of the copper-arsenic group, what would occur? If metallic iron had been placed in a similar solution, what would occur? If platinum were placed in the solution, what would occur?

126. One gram of pure iron wire is dissolved in sulfuric acid and diluted to 250 cc. How many cubic centimeters of potassium dichromate solution containing 5 grams per liter would be required to oxidize the ferrous sulfate in 50 cc. of the solution, as prepared above, to ferric sulfate?

127. 0.5 gram of arsenic trisulfide is dissolved in concentrated hydrochloric acid, 38 per cent HCl, specific gravity 1.19, by adding a few crystals of potassium chlorate, as described in Experiment 28. What volume of hydrochloric acid would be required?

128. (1) The solubility of lead sulfate at 18 degrees is 0.041 grams per liter. If the degree of ionization is 92 per cent, calculate the solubility-product constant. (2) If the solubility of lead chromate is 0.000026 grams per liter and the degree of ionization is 100 per cent, what is the solubility-product constant? (3) Could lead ion (Pb^{++}) be precipitated as lead chromate in a saturated solution of lead sulfate?

129. If a copper-arsenic-group unknown is known to contain no copper, how may the analysis be shortened? If it is known to contain only copper-group metals, how may it be shortened? If it is known to contain no lead, how may it be shortened?

130. An unknown solution is known to contain only one member of the arsenic group. Could the analysis be shortened? How?

131. A solution known to contain only one element gives a precipitate with sodium hydroxide which is soluble in an excess of the reagent. How would you proceed with the analysis?

132. If the residue left when the copper-group sulfides are treated with nitric-acid is not soluble in aqua regia, can it be mercury? What is it, probably? If the nitric-acid residue is not black, can it be mercury?

133. If an unknown solution is alkaline, what substances might be precipitated upon the addition of hydrochloric acid to precipitate the silver group? Why do we first acidify with nitric acid? Why could sulfuric acid not be used?

134. An unknown solution, known to contain no members of the silver group, gives a white precipitate when hydrochloric acid is added. What do you suspect the precipitate to be? Would you have to modify your method of analysis?

135. If considerable nitric acid is added to a silver-group unknown solution, and then an excess of hydrochloric acid, and the solution boiled, what effect may it have on some of the metals? How would you test for the elements so effected?

136. Why is it best to precipitate the silver group from the cold solution? If you heated the solution, what element would not precipitate? Where would you find it?

137. If you added ammonium hydroxide to a silver-group precipitate before washing out the lead chloride, what would be the result? What would you do to complete the analysis?

138. A saturated solution of silver chloride is made 0.1 molar with respect to sodium chloride. Assume the sodium chloride 85 per cent ionized and the silver chloride 100 per cent. If the solubility of silver chloride is 1.5×10^{-4} grams per liter, would the silver chloride precipitate when the sodium chloride is added, and what change in the concentration of the silver ion would occur?

139. (1) The solubility of silver sulfide is 2×10^{-5} grams per liter. Assume the silver sulfide in a saturated solution 100 per cent ionized, and calculate the solubility-product constant. (2) By comparing with the solubility-product constant of silver chloride, determine what concentration of chlorine ion (Cl^-) would be required to precipitate silver chloride from a saturated solution of silver sulfide?

140. Using the table on page 43, determine the ratio of the concentrations of the sulfide ion present in saturated solutions of copper sulfide and zinc sulfide. Assume both sulfides completely ionized.

141. During analysis one gram of the sulfides of the copper group was obtained, containing 40 per cent lead sulfide, 30 per cent copper sulfide, and 30 per cent mercuric sulfide. How many cubic centimeters of dilute nitric acid, 20 per cent HNO_3, specific gravity 1.1, will be required to dissolve the soluble sulfides?

142. During analysis 2 grams of precipitate for the iron-zinc group was obtained, containing 30 per cent chromium hydroxide, 30 per cent ferrous sulfide, 30 per cent manganese sulfide, and 10 per cent nickel sulfide. (1) What volume of dilute hydrochloric acid, 7.29 per cent HCl, specific gravity 1.036, would be required to dissolve the soluble part of the precipitate? (2) What weight of sodium peroxide would be required to change the chromium chloride formed in (1) to sodium chromate? (Only that part of the sodium peroxide actually taking part in the reaction is considered.) (3) If an excess of sodium peroxide were used in (2), what weight of ferric hydroxide would be formed? (4) If the analysis were continued as directed in the outline (p. 56), what weight of permanganic acid ($HMnO_4$) would be in the solution which forms the final test for manganese?

143. Given a solution containing silver, copper, and zinc, outline how you separate and identify each metal.

144. Given a solution containing arsenic, bismuth, iron, and barium, outline how you would separate and identify each metal.

145. A known solution contains lead, chromium, cobalt, and calcium. Show how you would separate and identify each metal.

146. Given a solution containing cadmium, zinc, aluminium, and magnesium, show how you would separate and identify each element.

147. Given a solution containing tin, mercury (mercuric), manganese, and ammonium, outline how you would separate and identify each element.

148. Why is sodium carbonate added to a solution before testing for the acid ions? What tests might be interfered with if this were not done?

149. Why should the filtrate from the sodium-carbonate precipitate be neutralized before testing for sulfuric acid with barium chloride?

150. If a solid substance gives a gas when treated with dilute sulfuric acid, what acids might be present? If the gas is odorless and colorless, what acid might be present? How would you prove it?

151. If a solution gives no precipitate with magnesium mixture, what acids are absent?

152. A water solution of an unknown substance is found to contain silver, copper, zinc, and barium; what acids cannot be present?

153. A water solution of an unknown substance is found to contain the sulfate ion; what metals cannot be present?

154. An unknown solid is found to contain the carbonate ion. If it is completely soluble in water, what metals are absent?

155. A water solution of an unknown substance contains the phosphate ion; what metals cannot be present?

156. If analysis shows that an unknown substance which is completely soluble in water contains iron, aluminium, zinc, strontium, and potassium, what acid ions must be absent?

157. An unknown solution which contains a sulfate is insoluble in water, but dissolves in dilute hydrochloric acid; what metals are sure to be absent?

158. If you were given a solid unknown, how would you proceed with it to get ready to begin the analysis?

159. Given a solid metal or alloy, how would you proceed with it?

160. What acid would you use to dissolve an alloy which is given you for analysis? If you used hydrochloric acid what difficulties might arise?

161. An unknown which is given you is insoluble, or only partially soluble, in water; how would you proceed to get it into solution?

162. Why is the following report on an unknown evidently wrong? White solid, partially soluble in water, completely soluble on the addition of a few drops of dilute hydrochloric acid. Found lead, bismuth, aluminium, zinc, barium, potassium, chloride, sulfate, acetate.

INDEX

91

PERIODIC SYSTEM OF THE ELEMENTS

H(1) 1.008

Period	Group O	Group I — A R_2O	Group I — B RH	Group II — A RO	Group II — B RH_2	Group III — A R_2O_3	Group III — B RH_3	Group IV — A RO_2	Group IV — B RH_4	Group V — A RH_3	Group V — B R_2O_5	Group VI — A RH_2	Group VI — B RO_3	Group VII — A RH	Group VII — B R_2O_7	Group VIII RO_4
1	He(2) 4.0	Li(3) 6.94		Be(4) 9.1		B(5) 11.0			C(6) 12.005	N(7) 14.01		O(8) 16.0		F(9) 19.0		
2	Ne(10) 20.2	Na(11) 23.0		Mg(12) 24.32			Al(13) 27.1		Si(14) 28.3	P(15) 31.04		S(16) 32.06		Cl(17) 35.46		
	A(18) 39.88	K(19) 39.1		Ca(20) 40.07		Sc(21) 44.1		Ti(22) 48.1			V(23) 51.0		Cr(24) 52.0		Mn(25) 54.93	Fe(26) 55.84 Co(27) 58.97 Ni(28) 58.68
3	Kr(36) 82.92		Cu(29) 63.57		Zn(30) 65.37		Ga(31) 69.9		Ge(32) 72.5	As(33) 74.96		Se(34) 79.2		Br(35) 79.92		
		Rb(37) 85.45		Sr(38) 87.63		Yt(39) 88.7		Zr(40) 90.6			Cb(41) 93.1		Mo(42) 96.0		—(43)	Ru(44) 101.7 Rh(45) 102.9 Pd(46) 106.7
4	Xe(54) 130.2		Ag(47) 107.88		Cd(48) 112.40		In(49) 114.8		Sn(50) 118.7	Sb(51) 120.2		Te(52) 127.5		I(53) 126.92		
		Cs(55) 132.81		Ba(56) 137.37		La(57) 139.0		Ce(58) 140.25								
5	Rare Earth Elements (59–72)															
6	Nt(86) 222.4		Au(79) 197.2		Hg(80) 200.6		Tl(81) 204.0		Pb(82) 207.2	Bi(83) 208.0	Ta(73) 181.5	Po(84) 210.0	W(74) 184.0	—(85)	—(75)	Os(76) 190.9 Ir(77) 193.1 Pt(78) 195.2
		—(87)		Ra(88) 226.0		Ac(89) ——		Th(90) 232.4			Bv(91) 234.2		U(92) 238.2			

			OMIC EIGHT
Alumin	APR 21 1942 P	MAY 1 1 1967 20	6.0
Antimo			4.3
Argon			0.2
Arsenic		RECEIVED	8.68
Barium	JUN 3 1948		2.4
Bismuth			4.01
Boron		APR 2 7 '67 -2 PM	0.9
Bromine	1 May'53 DM		6.00
Cadmiu			3.7
Cæsium	APR 7 1953	LOAN DEPT.	1.04
Calcium			5.2
Carbon			9.10
Cerium			0.9
Chlorine			6.0
Chromi	1 Jun'54 BMY		2.9
Cobalt			5.45
Columbi	MAY 1 8 1954 LU		1.7
Copper			0.4
Dysprosi	25 Feb'56 KC		1.1
Erbium	FEB 1 1 1956 LU		0.2
Europiu			3.3
Fluorine			7.88
Gadolini	27 MAY 58 IZ		6.00
Gallium			7.63
Germani			2.06
Glucinu			.5
Gold	REC'D LD		.5
Helium			.2
Holmium			.0
Hydroge	MAY 1 5 1958		.4
Indium			.5
Iodine			.7
Iridium	10 Feb'59 M R		.1
Iron			.0
Krypton	REC'D LD		.2
Lanthan			.0
Lead	JAN 27 1959		.2
Lithium			.5
Lutecium			5.7
Magnesiu		LD 21–100m-7,'39(402s)	5.37
Mangane			00.6
Mercury	Hg	200.6	